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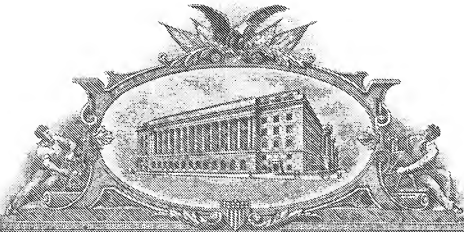Document type: Certified copy of priority document

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PROVISIONAL APPLICATION FOR PATENT COVER SHEET

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TITLE OF THE INVENTION (500 characters max)

MATERIAL AND DEVICE PROPERTIES MODIFICATION BY ELECTROCHEMICAL CHARGE INJECTION IN ABSENCE OF CONTACTING ELECTROLYTE FOR EITHER LOCAL SPATIAL OR FINAL STATES

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The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.

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Respectfully submitted,

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PROVISIONAL APPLICATION COVER SHEET
Additional Page

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MATERIAL AND DEVICE PROPERTIES MODIFICATION BY ELECTROCHEMICAL CHARGE INJECTION IN THE ABSENCE OF CONTACTING ELECTROLYTE FOR EITHER LOCAL SPATIAL OR FINAL STATES

BACKGROUND OF THE INVENTION

This invention was made with partial Government support under Contract No.
5   MDA972-02-C-0044 awarded by the Defense Advanced Research Projects Agency.
The Government has certain rights in this invention.

Field of the Invention

This invention relates to tuning the electronic, magnetic, and optical properties of
10   materials and devices by non-faradaic electrochemical charge injection. Such tuned
properties are developed either in the presence or absence of contacting electrolyte,
and necessarily maintained in the absence of contacting electrolyte. Applications of the
charge injection and associated magnetic, optical, and electronic properties changes
are for such uses as optically transparent electronic conductors; catalysis; fuel cells;
15   spintronic devices; information storage devices; nanostructured magnets; sensors;
electromechanical actuators; the control of thermal and electrical energy transport; the
tuning of surface energy and friction; the switching, phase shift, and attenuation of
electromagnetic radiation; tuning magnetoresistive materials; and drug delivery.

20   ### Description of the Background Art

It is well known that charge injection can change the magnetic, electronic and
optical properties of materials. Prior-art methods for changing these material properties
by charge injection either (1) involve gate-based charge injection across a dielectric (so
charge injection is limited by dielectric breakdown), (2) require the presence of a
25   surrounding electrolyte for the transformed material (thereby limiting device
applicability), or (3) use dopant intercalation (thereby limiting applicable materials and
providing problematic structural changes). These three methods are called **dielectric-**

based charge injection, **non-faradaic electrochemical** charge injection, and **faradaic electrochemical** charge injection, respectively.

   Dielectric-based charge injection is used for transistor devices that are critical for both today's electronic circuits and those proposed for the future. In these transistor
5   devices, current is carried through a semiconductor between source and drain electrodes. The current through this semiconductor (channel) is controlled by charge injection into the semiconductor channel by application of a voltage between the source electrode and the gate electrode, which is separated from the semiconductor channel by a dielectric. This charge injection is that of an ordinary dielectric capacitor, so the
10 amount of charge injection that can be achieved is limited by the breakdown strength of the dielectric. While enormously useful for submicroscopic electronic devices, this dielectric-based charge injection is unsuitable for macroscopic charge injection in materials having macroscopic external dimensions. X.X. Xi $et.al.$ (Applied Physics Letters **59** 3470 (1991)) have demonstrated dielectric-based switching of the
15 superconducting transition temperature (T_c) of films of $YBa_2Cu_3O_{7-x}$ over 2 K range. The achieved resistance modulation in the normal state can be as much as 20% in normal state and 1500% near T_c. Using a similar method of dielectric-based charge injection in the $YBa_2Cu_3O_{7-x}$ superconductor, J. Mannhart et $al.$ (Applied Physics Letters **62**, 630 (1993)) demonstrated that T_c can be changed by up to 10 K. However, the dielectric-
20 based method of T_c switching used by Xi et $al.$ and by J. Mannhart et $al.$ is not applicable for a macroscopically thick superconducting material.

   Non-faradaic electrochemical charge injection uses nanostructured materials having very high surface area and is applicable for from nanosize to bulk materials. However, prior-art technologies teach that this charge injection can only be
25 accomplished by developing and maintaining contact of the electrolyte with regions of the material where charge injection is desired, which for macroscopic nanoporous materials includes internal surfaces. In other words, the prior art teaches that non-faradaic electrochemical charge injection into a material requires maintained contact of that material with the electrolyte. This non-faradaic electrochemical charge injection has
30 been used to provide electrochemical electromechanical actuators (artificial muscles,

see R. H. Baughman *et al.*, *Science* **284**, 1340 (1999), R. H. Baughman *et al.*, U.S. 6,555,945) and liquid-ion-gated FETs (field-effect transistors, see M. Krüger, Applied Physics Letters 78, 1291-1293 (2001)). However, the maintained contact between the electrode (including both internal and external surfaces) and the electrolyte limits

5   applicability of prior-art methods of non-faradaic electrochemical charge injection. For example, the surrounding electrolyte for the above described liquid-ion-gated FETs limits their applicability for gas state sensing – since a sensed gas must dissolve in the electrolyte before it can be detected, which decreases both device response rate and sensitivity. Likewise, non-faradaic electrochemical charge injection has been used to

10 enhance the catalytic activity of electrode materials for the chemical transformation of materials present in the electrolyte. However, the prior-art use of pervasive electrode contract with the electrode has eliminated the possibility of using charge injection to optimize catalyst activity for gas phase chemical reactions. In addition, non-faradaic electrochemical charge injection provides the basis for supercapacitors having much

15 larger charge storage capabilities than ordinary dielectric supercapacitors. In the prior art (K. H. An *et al.*, *Adv. Funct. Mater.* **11**, 387 (2001) and C. Niu, E. K. Sickel, R. Hoch, D. Moy, H. Tennent, *Appl. Phys. Lett.* **70**, 1480 (1997)), these supercapacitors are kept in the charged state as a result of maintained contact between the nanostructured electrodes and the electrolyte. Since the electrolyte provides mechanisms for self-

20 discharge, long term energy storage in such a supercapacitor is not possible. Also, the possibility of charging non-faradaic supercapacitors, removing the electrolyte, and then storing energy in the dry-state supercapacitors was not conceived.

Faradaic electrochemical charge injection involves the intercalation of ions into a solid electronically conducting electrode material. This method is limited to the types

25 of materials that can incorporate dopant by a reversible process, preferably at room temperature. For example, elemental metals and metal alloys cannot undergo charge injection by this method. Similarly, this method of charge injection is not useable for non-porous materials having three-dimensional covalent bonding. Also, substantial dopant intercalation fundamentally changes the structure of the material and can

30 introduce gross structural defects. As a consequence, dedoping does not completely

return the material to the original state. Nevertheless, the faradaic electrochemical method of charge injection has great value, as indicated by the year 2000 award of a Nobel prize for the discovery that dopant intercalation (either chemically or electrochemically) into semiconducting conjugated polymers can convert these semiconductors into metallic conductors. Faradaic electrochemical doping (for conducting polymers and other materials) is used for both primary and rechargeable batteries (Y. Gofer *et al.*, Applied Physics Letters **71**, 1582-1584 (1997)), conducting polymer actuators (R. H. Baughman, Synthetic Metals **78**, 339 (1996)), electrochromic displays (W. Lu *et al.*, Synthetic Metals **135-136**, 139-140 (2003)), and electrochemical light emitting displays (G. Yu *et al.*, Science **270**, 1789-1791 (1995)). For such devices, dramatic structural changes are typically associated with dopant intercalation, and these charges are not fully reversed on de-intercalation – which limits cycle life. The required dopant insertion and de-insertion processes (called intercalation and de-intercalation) result in slow device response, short cycle life, hysteresis (leading to low energy conversion efficiencies), and a device response that depends on both rate and device history.

The embodiments of the present invention eliminates key problems of these prior-art technologies, by showing that non-faradaic electrochemical charge injection can be maintained, and even developed, for regions of the electrode that are not in contact with the electrolyte. The present discoveries enable materials and device applications that would not be possible, or would be less advantageous, in the presence of locally contacting electrolyte.

SUMMARY OF THE INVENTION

A *first object* of the invention is to provide processes for the combination of injecting charge in a material electrochemically via non-faradaic (double-layer) charging and retaining this charge and associated desirable properties changes when the electrolyte is removed.

A *second object* is to provide compositions and applications using material property changes that are induced electrochemically by double-layer charging and retained during subsequent electrolyte removal.

A *third object* is to provide reversible processes for electrochemically injecting charge into material that is not in direct contact with an electrolyte.

A *fourth object* is to provide devices and other material applications that use properties changes resulting from reversible electrochemical charge injection in the absence of an electrolyte. Examples of such application of charge injection and associated magnetic, optical, and electronic properties changes are for optically transparent electronic conductors; spintronic devices; information storage devices; nanostructured magnets; chemical and mechanical sensors; electromechanical actuators; the control of thermal and electrical energy transport; the tuning of surface energy and friction; the switching, phase shift, and attenuation of electromagnetic radiation; tuning magnetoresistive materials; and drug delivery.

Invention embodiments provide processes for improving material properties by non-faradaic charge injection and retaining these switched properties in the absence of electrolyte that contacts charge-switched electrode regions.

More specifically, the invention provides processes whose overall effect is to provide, retain and employ charge injection to substantially change the properties of a largely electrolyte-free porous material region A or particle A that comprises:

(a) immersing the A into an electrolyte;

(b) providing an ion conducting and substantially electronically insulating continuous path between the A and a counter electrode material B;

(c) applying a potential between the A and the counter electrode B for sufficient time that the desired charge is injected into the A; and

(d) substantially removing the electrolyte from contact with the A,

wherein both the A and counter electrode B have an electronically conducting charged or uncharged state and the A has an achievable capacitance for non-faradaic charging of above about 0.1 F/gm.

Composition of matter resulting from the above processes are also provided in the invention embodiments. An example is a composition of matter containing non-faradaically injected charge and substantially no electrolyte that maintains, in a suitable environment, a potential that deviates from the potential of zero change by at least 0.1 V.

Devices that utilize non-faradaic charge injection in the absence of locally contacting electrolyte are also provided in invention embodiments. These devices having a tunable response comprise:

(a) a nanostructured electrode component C of a first electrochemical electrode and a electrode component D of a second electrochemical electrode;

(b)   an ionically conducting material that is substantially electronically non-conducting that connects said first and said second electrochemical electrodes; and

(c) means to provide a voltage between said first and said second electrochemical electrodes,

wherein the electrode component C is not in direct contact with an electrolyte, the electrode component C has an achievable capacitance of above about 0.1 F/gm for substantially non-faradaic charging, and wherein properties changes of the electrode component C in response to injected charge are used to achieve device performance.

Further scope of applicability of the present invention will become apparent from the detailed description given hereinafter. However, it should be understood that the detailed description and specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention will be more clearly understood and further applications will be apparent when reference is made to the following detailed description of preferred embodiments of the invention that are given by way of illustration only, and thus are not limitative of the present invention, and wherein:

Figure 1 shows the observed tunability of four-point electrical conductivity as a function of applied potential (versus Ag/Ag+) for a sheet of single-wall carbon nanotubes immersed in an organic electrolyte (0.1M tetrabutylammonium hexafluorophosphate in acetonitrile). The different curves are for three successive cycles of electrochemical potential change (using squares, circles, and triangles for successive cycles).

Figure 2 shows the dependence of four-point electrical conductivity upon the amount of injected charge (per carbon) for the nanotube sheet used for the Figure 1 experiment (black data points are for experiments using 0.1M tetrabutylammonium hexafluorophosphate/acetonitrile electrolyte and near-white data points are for related measurements using 1 M aqueous NaCl electrolyte). The origin of the charge scale is arbitrary.

Figure 3 shows measured cyclic voltametry for the SWNT sheet of Figures I and 2 when immersed in tetrabutylammonium hexafluorophosphate electrolyte. These results show that the charging is predominately non-faradaic by double-layer charge injection.

Figure 4 shows that the dramatic hole-injection-induced increase in electrical conductivity of the nanotube sheet in Figure 1 and 2 is largely retained when the hole-injected electrode is dried in flowing dry nitrogen atmosphere to remove the electrolyte. The insert to this figure shows results for the initial four-hour period on an expanded time scale.

Figure 5 shows the retention of conductivity enhancement when the nanotube sheet is removed from the electrolyte and held in air for the investigated five day period.

Figure 6 provides cyclic voltametry measurements (20 mV/sec using 1 M aqueous NaCl electrolyte) for nanostructured platinum electrodes, showing that charging is non-faradaic by double-layer charge injection.

Figure 7 shows potential measurements before and after removal of the nanostructured Pt electrodes of Figure 6 from the 1 M NaCl aqueous electrolyte (and subsequent reimmersion into the electrolyte). The measured electrode potentials of both positive and negative electrode indicate that non-faradaically injected charge is partially retained even when the electrodes are removed from the electrolyte.

Figure 8 shows a scanning electron microscope (SEM) picture of a nanostructured inverse-opal carbon electrode that we find stores charge without the need for a surrounding electrolyte.

Figure 9 uses carbon nanotube electrodes to schematically illustrate means used in invention embodiments for injecting charge into regions of a high-surface-area electrode that is not directly contacted with electrolyte.

Figure 10 schematically illustrates a prior-art device technology for using electrochemical double-layer charge injection to switch the conductivity of a semiconducting channel material. This device uses liquid-ion gating.

Figure 11 schematically illustrates a first electrochemical transistor device of the present invention that does not use liquid-ion gating, which could be used for information storage, electronic switching, or gas sensing.

Figure 12 schematically illustrates a second electrochemical transistor device of the present invention that does not use liquid-ion gating, which could be used for information storage, electronic switching, or gas sensing.

Figure 13 schematically illustrates an optical gas sensor, based on the surface-enhanced Raman effect, that uses electrochemically controlled charge injection in a metallo-dielectric photonic crystal to optimize sensitivity and species selectivity.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Invention embodiments are directed to processes, materials, and devices that utilize non-faradaically injected charge and associated changes in either magnetic, electronic, optical, or chemical properties, wherein the non-faradaically injected charge
5   is retained in the absence of direct or maintained contact with the electrolyte.

Differentiation between faradaic and non-faradaic charging processes is generally important for understanding the advantages and novelty of these invention embodiments. Significant amounts of electronic charge can be injected (i.e., stored) in an electrode typically only if counter ions of opposite charge are available in close
10   proximity to the electronic charge injected into the electrode. These counter ions can compensate the electrostatic repulsion of the electronic charges on the electrode, thereby enabling the electronic charge injection process to proceed to high levels. A faradaic process for an electrode material is one in which electronic charge injected into the electrode is predominately compensated by ions that are inserted (i.e., intercalated)
15   into the volume of the charge-injected component of the electrode. A non-faradaic process is one in which compensation of electronic charge on the electrodes is by ions that do not enter the solid volume of the charge-injected component of the electrode. A well-known example of a non-faradaic process is one in which the counter ions (to the electronic charge on the electrodes) are located in the electrolyte (within the so-called
20   charge double layer). Evidence of faradaic charging processes is provided by the existence of peaks in cyclic voltamograms (current-versus-potential plots at constant potential scan rates). In contrast, the current in a cyclic voltamograms only weakly depends on potential in a potential range where electrode charging is non-faradaic and the electrolyte is neither reduced nor oxidized.

25   Prior-art understanding of non-faradaic charge injection is that the gravimetric capacitance (and therefore the non-faradaic charge injection capability for an electrode) is given by the following equation: $C_g = A_g C_s$. In this equation, C_s is the capacitance per unit surface area of the conducting component of the electrode when this surface area is in contact with electrolyte. A_g is the total surface area of the electronically conducting
30   component of an electrode that is in contact with suitably thick layer of electrolyte,

normalized to the weight of the electronically conducting component of the electrode. This electrode surface area includes all electrolyte-coated internal and external surface area of the electronically conducting component of the electrode. Ignoring the potential dependence of C_s, the gravimetric density of injected charge (per weight of the electronically conducting component of the electrode) is $q_g = (V-V_o)C_g$, where V_o is the potential at which there is zero electronic charge injected in the electrode and V is the potential applied to the electrode, measured with respect to the same reference electrode as V_o. We have discovered that these equations are not generally valid when only part of a nanostructured electrode is in contact with the electrolyte. The processes that lead to violation of these equations are the basis for embodiments of this invention.

More specifically, we have discovered that dopant ions (together in some instances with solvating species from the electrolyte) can migrate from the electrolyte (solid-state or liquid) to regions of the electrode that are not coated with electrolyte. This dopant ion migration enables electronic charge to be injected in regions of the electrode that are not in contact with the electrolyte, thereby increasing the injected charge (q_g) above the values given by the equation given in the last paragraph. Most important for device applications, such as field emission displays, our discovery means that we can use electrochemical double-layer charge injection to inject charge in regions of the electrode that are in a gas or vacuum, rather than in an electrolyte.

This enabling discovery resulted from our surprising observation that charge can be non-faradaically injected into an electrode, and then retained in this electrode when this electrode is removed from a volatile electrolyte and dried by pumping in dynamic vacuum. This observation means that we can tune the optical, magnetic, and electronic properties of an electrode material, and then substantially maintain these tuned properties for materials applications in ambient, where the problematic electrolyte is absent.

Also generally important for invention embodiments, the stability we observe (in the absence of electrolyte) for injected charge on nanostructured materials surfaces (internal and external) indicates that we can continuously vary the degree of charge injection in nanostructured material elements that are not in direct contact with the

electrolyte or any other ion-containing material. This stability and the continuous tunability of charge injection in the absence of direct electrolyte contact enables many of the materials and device applications in the device embodiments. These embodiments require that the continuous tuned material elements are electronically
5   connected to an electrode, so electronic part of charge injection can occur. Also, they require that ion conduction path exist or can self form to the continuously tuned elements – which need not be in direct contact with the electrolyte.

Processes of our invention require at least two electrodes, called working and counter electrodes. For the case where the desired charge-injection-produced
10 properties changes are for only one of these electrodes, the working electrode is defined as this electrode. In addition, one can optionally employ a reference electrode, whose function is to place the potentials of the working and counter electrodes on an absolute scale. The working electrode should preferably have a capacitance of at least 0.1 F/gm when fully immersed in electrolyte. More preferably, the capacitance of the
15 working electrode fully immersed in the electrolyte should exceed 1 F/gm. Most preferably, the capacitance of the working electrode should exceed 10 F/gm when fully immersed in electrolyte. The specific capacitance of an electrode is optionally and preferably derived using the conventional method from the voltage scan rate dependence of the slope of specific current versus voltage (versus a reference
20 electrode). The above specific capacitances for the preferred, more preferred, and most preferred invention embodiments are the maximum values that can be measured in the stability range of the electrolyte.

Before discussing particular embodiments of our invention, we will describe surprising observations that we have made, which provide the basis for these
25 embodiments. These discoveries are further elaborated in the examples section. After this we will elaborate on (1) specialized invention embodiments and (2) preferred and optional material components and processing methods for the practice of these embodiments.

The results in Figures 1 and 2 show that a potential change and corresponding
30 electrode charge injection can dramatically change the properties of a nanostructured

electrode material. Figure 1 shows the presently observed continuous tunability of four-point electrical conductivity as a function of applied potential (versus Ag/Ag+) for a sheet of single-wall carbon nanotubes (SWNTs) immersed in an organic electrolyte (0.1M tetrabutylammonium hexafluorophosphate in acetonitrile). These results

5   demonstrate that the electrical conductivity of the nanotube sheet can be increased by about an order of magnitude by electrochemical charge injection. There is slight hysteresis evident for the curves in Figure 1, with the conductivity σ on the extreme left side of the potential minimum slightly higher for hole injection (increasingly positive applied potential) and the conductivity slightly lower on the extreme right side of the

10   minimum for electron injection (increasingly negative applied potentials). The different curves are for three successive cycles (using squares (101), circles (102), and triangles (103) for successive cycles). The density of these nanotube sheets is about 0.3 gm/cm^3, versus the density of about 1.3 gm/cm^3 for densely packed nanotubes having close to the observed average nanotube diameter. Hence the void volume in these

15   nanotube sheets is about 76.9 volume percent. This high void volume, and the correspondingly high accessible surface area, is generally important for achieving high degrees of non-faradaic change injection at modest applied potentials. Supporting this conclusion, the measured BET surface area determined from nitrogen gas adsorption for these nanotube sheets is approximately 300 m^2/gm.

20   Figure 2 shows the dependence of four-point electrical conductivity upon the amount of injected charge for both the above experiment with 0.1 M tetrabutylammonium hexafluorophosphate/acetonitrile electrolyte (black data points(201)) and for other experiments using 1 M NaCl electrolyte (near-white data points(202)). Although not indicated here in this plot of conductivity versus charge

25   (because charge measurements are not reliable for potentials exceeding the redox stability of aqueous electrolyte), reversible conductivity increases from about 100 S/cm to about 1000 S/cm were also observed at positive potentials for experiments using the 1 M aqueous NaCl electrolyte. The origin of the charge scale is arbitrary. The charge per carbon at the minimum in electrical conductivity can be used to place origin of the

charge axis, since theory suggests that conductivity should be minimized at the potential of zero charge (pzc), where there is no charge on the carbon nanotube.

Figure 3 shows measured cyclic voltametry during charge injection for the above SWNT sheet when immersed in the above tetrabutylammonium hexafluorophosphate electrolyte. The absence of major peaks in this cyclic voltametry curve (measured versus Ag/Ag+) indicates that charging is predominately non-faradaic for this electrolyte and potential range.

Figure 4 shows that the dramatic increase in electrical conductivity of the nanotube sheet in Figure 1 and 2 (obtained by hole injection for the nanotube sheet and the organic electrolyte of these examples) is largely retained when the hole injected electrode is dried in flowing dry nitrogen atmosphere to remove the electrolyte. The insert to this figure (describing results over a four-day period) show first a conductivity increase and then a conductivity decrease during the first few hours of this four day study, which might be a result of volatilization of the acetonitrile from the solvent component of the organic electrolyte. Figure 5 shows the retention of conductivity enhancement when the nanotube sheet is removed from the electrolyte and held in air for the investigated five day period. These results show that the enhancement of electrical conductivity of the hole-doped nanotube sheet is relatively stable even in atmospheric air.

We found even more surprising results when tried to extend this results to generic nanostructured materials, and in particular to a nanostructured metal – which has no possibility or accommodating ions by faradaic processes (intercalation). These results are for platinum electrode made by compaction of 30 nm diameter Pt nanoparticles, using the method described by J. Weissmüller *et al.* in Science **300**, 312 (2003). The cyclic voltametry results in Figure 6 (using 1 M aqueous NaCl electrolyte) show that these electrodes provide the classical dependence of current on applied potential that arises for double-layer charging. There are no current peaks due to Faradaic processes and the current at constant voltage scan rate (20 mV/sec) varies little with potential. From plots of current versus potential scan rate in 1 M aqueous NaCl electrolyte), the electrode capacitance is about 14.5 F/gm. This high observed

volume fraction of void space in these pellets (between 81.6 and 87.2 volume percent for compaction pressures between 0.6 MPa and 2.1 MPa) and the corresponding high gravimetric surface area explains the high degree of non-faradaic charge injection that results for modest applied potential for the nanostructured Pt electrode.

5   Most important, we find that the nanoporous Pt electrode remains charged when disconnected from the power source and removed from the electrolyte. Our initial results indicating this stability are shown in Figure 7. As shown here, the charge on the positive electrode (i.e., the hole-doped electrode) is retained when the electrode is removed from the electrolyte, and then held in air. Indication of this retained charge is

10   provided by reimmersion of the nanoporous Pt electrode in the 1 molar NaCl electrolyte, and finding that the electrode potential is substantially unchanged. Just like the case for the carbon nanotube electrode, the potential of the negatively charged electrode is less stable than for the positively charged electrode, as indicated by the results shown in the lower part of this figure.

15   Since it is possible that some electrolyte is still retained inside the pores of the Pt electrode during the experiment of Figure 7, we repeated this experiment using much longer time periods when the electrodes are not in contact with the 1 M NaCl electrolyte, and dynamically pumping on the nanoporous Pt during this time period after the pellet electrodes have been disconnected from the power source and the electrolyte

20   was removed from the electrochemical cell. The electrode potentials (versus Ag/AgCl) before and after this two days exposure of the electrodes to dynamic pumping were +0.58 V and +0.45 V for the hole-injected electrode and -0.04 V and +0.02 for the electron-injected electrode. The potential between the two electrodes changed from the initial 0.62 V to a final 0.43 V after removal of the electrodes from the electrolyte and

25   dynamically pumping on these electrodes for two days.

        To further evaluate the stability of charge storage, we extended the time period in which we exposed the platinum pellets to dynamic vacuum to a week. After this, which we reimbursed the nanoporous Pt electrodes in the 1 M NaCl electrolyte to determine their charge state by electrochemical potential measurements (naturally,

30   without applying any external potential). High charge storage is again indicated for the

positively charged Pt electrode (indicated by retention of a 0.28 V potential, versus Ag/AgCl, compared with the initial potential before electrolyte removal of 0.33 V). The negatively charged electrode had lower stability, as indicated by a potential change from the initial -0.68 V (before removal of the electrolyte and the week-long process of

5   drying the electrode in dynamic vacuum) to a final potential on initial reimmersion into the electrolyte of –0.32 V.

Electron and hole injection in the nanostructured platinum samples does not significantly change electrical conductivity (in contrast with the case for the nanostructured nanotube sheets), since this charge injection causes only a small

10   fractional change in the already high total electron concentration. However, we demonstrate that hole-injection-induced change in unit cell volume of Pt nanocrystals (within the nanoporous Pt electrode) is retained after drying the Pt electrodes for two days in dynamic vacuum and during exposure to air (while x-ray diffraction measurements to determine unit cell parameters were made). The retained increase in

15   unit cell volume for the Pt nanocrystals in the positively charged electrode was quite large (1.20%). While it is known that charge injection in a liquid electrolyte can provide changes in unit cell volume, the prior art did not anticipate that these charge-induced volume changes can be retained in electrolyte-free materials (J. Weissmüller et al., Science **300**, 312 (2003) and R. H. Baughman, Science **300**, 268-269 (2003)).

20   The implication of these results for practical applications in invention embodiments are profound, since diverse properties (including superconductivity, magnetism, and magneto-resistance) can be very sensitive to material volume.

We have also shown experimentally that inverse opals of conducting materials are another type of composition that we can use for invention embodiments. In these

25   experiments a carbon inverse opal was synthesized by infiltration of phenolic resin into an ordinary SiO_2 opal, pyrolizing this phenolic resin, and then removing the SiO_2 template material by dissolution in HF solution. A scanning electron microscope (SEM) image of this carbon inverse opal is shown in Figure 8. Experiments done in both 1 M aqueous electrolyte and tetrabutyl ammonium hexafluorophosphate/acetonitrile

30   electrolyte show that electrochemically injected charge are partially retained when the

electrodes are removed from the electrolyte and dried, and that the stability of injected charge is much higher than for the same electrodes immersed in the electrolyte with the power source disconnected.

5   This indicated retention of electrochemical double-layer-injected charge and charge-injection-induced properties charges, when the charge-injected material is not in contact with the electrolyte, is more broadly important for invention embodiments. Also important, we find that dry-state-retained injected charge is highly mobile, as evidenced by our observation that the charge on dry negatively and positively charged nanostructured electrodes rapidly occurs when these electrodes are contacted in the

10   dry state.

We next describe processes, materials, and device applications leading from our discovery of means for electrochemically injecting charge in nanostructured materials and retaining this injected charge when the nanostructured material is not in contact with the electrolyte. These applications use our discoveries that non-faradaically

15   injected charge (and associated properties changes) are retained in the absence of electrolyte. Use is also made of our discovery that non-faradaically injected charge (ion and corresponding electronic countercharge) of electrolyte-free electrode can be highly mobile. Because of this mobility of the ions and electronic charge, we can reversibly and controllably electrochemically inject electronic charge and counter ions in

20   nanostructured material elements that are not placed in direct contact with an ion source (for example, an electrolyte or intercalated material, such as a doped conducting polymer).

Both here and elsewhere herein the terms "free of electrolyte", "not directly contacted with electrolyte", "not contacted by the electrolyte", "largely electrolyte free",

25   and like terms have a specific meaning that we now define. These terms apply for a material element α if any one of the following cases applies: (1) Material component α was at no point placed in physical contact with a bulk electrolyte composition employed for either processing, device fabrication, or device operation; (2) Either anions, cations, and/or solvating species are present only in 10 nm or thinner surface layers on or within

30   material component α or as salt crystals on or within material component α that can not

serve as an effective electrolyte under application conditions; (3) Electrolyte-derived chemical species in materials component α that can be almost entirely removed from the bulk electrolyte by pumping in dynamic vacuum at room temperature are essentially stable in materials component α under the same conditions; (4) The ratio of free anions

5 to free cations that are present in materials component α (i.e., those that are not crystallized as salt crystals) is either lower than 0.9 or above 1.1; and (5) major components in the utilized electrolyte are substantially absent in materials component α. Defining the meaning of these terms and like terms is pertinent, since the devices of invention embodiments operate by the surface diffusion of ions from the electrolyte and

10 such ion diffusion can be accompanied by co-diffusion of ion solvating species from the electrolyte.

We first consider the process of our invention in which we tune the properties of a nanostructured material by non-faradaic charge injection in an electrolyte, and retain these properties changes and associated injected charge when the electrode is free of

15 electrolyte. In the simplest embodiment of this process, which is optional and most preferred, the material to be processes by electrochemical charge injection is immersed into a liquid electrolyte that is based on a volatilizable solvent (like water or acetonitrile). This material component is used as the working electrode of an electrochemical cell that comprises this working electrode and a counter electrode. Optionally and

20 preferably, a reference electrode is also present in this electrochemical cell, since measurement of the potential of this working electrode with respect to this reference electrode can be used to regulate the charge injection process. This nanostructured material, containing electrolyte in its pore structure, is charged by application of a potential difference between working and counter electrodes. Satisfactory completion of

25 the desired degree of charge injection can be monitored by measuring either the total charge passed through the electrochemical cell or the evolution of electrode potential versus a reference electrode. After charge injection, the nanostructured electrode (or electrodes) in which charge injection is needed can be disconnected from the power source and then dried or otherwise processed to remove liquid electrolyte (such as by

30 washing in the solvent component of the electrolyte, followed by drying). In order to

retain injected charge in the dried electrode, it is generally important that the electrode material is not contacted with materials that can undergo redox reactions with charge on the electrode. Avoiding such degradative reactions is typically more difficult to handle for electron-injected electrodes than it is for positively injected electrodes, although this problem is decreased in difficulty when the degree of charge injection in the electrode is not high.

More generally, a process of invention embodiments is described for providing, retaining, and employing charge injection to substantially change the properties of a largely electrolyte-free porous material region A. This process comprises: (a) forming an electrolyte within the interior of A, (b) providing an ion conducting and substantially electronically insulating continuous path between A and a counter-electrode material B, (c) applying a potential between A and counter electrode B for sufficient time that the desired charge is injected into A, and (d) substantially removing the electrolyte from A, wherein both A and B have an electronically conducting charged or uncharged state and A has an achievable capacitance for non-faradaic charging of above about 0.1 F/gm.

The electrolytes used for process step (a) can be any of the many aqueous and organic electrolytes latter described. While solid-state electrolytes can be employed, they are less preferable than liquid electrolytes having electrolyte components that are easily volatilized in step (d) of the process. Electrolytes having high redox stability (such as below listed ionic liquids) are optionally and especially preferred when high degrees of electrode charge injection are needed. The optional and preferred composition of material A depends upon the intended use of the charge-injection modified material, and these compositions for various applications will be later elaborated. The composition of electrode B is relatively unimportant unless the charging of this electrode is desirably used for the production of material that is oppositely charge injected to that of electrode B. If the function of electrode B is merely to provide a counter-electrode to material A, the capacitance of this electrode is preferably at least twice that of electrode A, so that most of the applied potential between electrode A and electrode B is applied across electrode A. The potential applied during step (c), the time evolution of this

potential, and the duration of this potential depends upon the redox stability window of the electrolyte and whether or not redox processes occurring in the electrolyte will harmfully degrade either the electrolyte or the electrodes. It is simplest to use either constant current or a constant inter-electrode potential between electrode A and electrode B. However, it is optional and preferable for maximizing rate for batch materials processing that resistance compensation be used to control the inter-electrode potential, so order to both rapid charge injection occurs and damage to either the electrodes or electrolyte due to excessive applied potentials is avoided. J. N. Barisci *et al.* (Journal of Smart Materials and Structures **12**, 549-555 (2003)) describe the use of resistance compensation for another use (electrochemical electromechanical actuators), and the concepts described by these authors are applicable for the present application.

Processes of invention embodiments for employing charge injection to substantially change the properties of a largely electrolyte-free porous material can be applied to various forms of these materials, such as sheets, fibers, and powders. Various methods can be used for convenient non-faradaic electrochemical charge injection into powders, such as nanotube powders. A first method is to assemble these powders into a solid electrode form, such as a sheet, use this sheet as an electrode for predominately non-faradaic charge injection, and then to break these sheets into powders, such as by using well-known ultrasonication processes. Unless practiced carefully, this method can potentially result in degradation of charge on the carbon nanotubes.

A second method is to disperse the powder in electrolyte in at least one compartment of a separated-compartment electrochemical cell (where the anode compartment and cathode compartments are separated by either a ion conducting membrane or a porous frit). Agitation of the dispersion of powder in the electrochemical cell (such as by stirring) brings the powder particles or fiber into intermittent contact with the electrode of this compartment, thereby permitting non-faradaic charging of the powder. The opposite compartment of this electrochemical cell can have conventionally shape electrode (such as a sheet) and can optionally also contain an agitated

electrolyte-dispersed powder that can be either the same or different from the powder in the other cell compartment. An advantage of this arrangement is that two powder samples can be charged (albeit with opposite charge) during the charging step of the process.

5   A third method is to use a moving conducting belt to carry the powder into and out of the electrochemical cell, wherein this moving belt is part of the electrode. The opposite electrode (optionally and most preferably in a separate electrode compartment) can either include a conventionally configured electrode (such as a sheet), or can contain the same type as belt-electrode powder delivery system as for the other mentioned electrode.

10   A fourth method is to disperse the powder in the electrolyte of an electrode compartment, and to configure this compartment so that the effect of gravity is to provide contact between the powder and the electrode of this compartment (which is optionally and preferably a planar electrode). In this method the electrolyte is selected to be either substantially heavier or substantially lighter than the powder. In the former case the electrode of the compartment is in the lower most region of the electrolyte compartment and in the latter case the electrode is in the upper most region of this compartment.

15   Materials used for properties tuning by non-faradaic charge injection optionally and preferably have an achievable gravimetric capacitance for predominately non-faradaic charging that is preferably above about 0.1 F/gm, more preferably above about 1 F/gm, and most preferably above about 10 F/gm. By achievable gravimetric capacitance we mean the capacitance measured when using an electrolyte and potential range that maximizes non-faradaic charging and still yields predominately non-faradaic charging. The gravimetric surface area of the materials used for properties tuning by non-faradaic charge injection have an achievable gravimetric surface area (measured in nitrogen gas using the standard Brunauer-Emmett-Teller, BET, method) of preferably above about 0.1 m^2/gm, more preferably above about 5 m^2/gm, and most preferably above about 50 F/gm.

Diverse properties can be tuned, and in many cases dramatically changed, as a consequence of the above process for electrochemically injecting charge non-faradaically and retaining this charge in the electrolyte-free state. Some of the effects by which charge injection can change material properties are: (1) the direct effect of changing band filling, (2) the effect of volume expansion and associated dimensional change due to charge injection, and (3) the effect of creating surface dipoles involving the injected electronic charge and correlated ions on the material surface.

Physical properties, such as electrical conductivity, optical absorption, magnetization, magnetoresistance, electromagnetic shielding properties, and the critical temperature of superconducting transition (T_c) depend very strongly on the number of charges carriers at the Fermi level. Optional and preferred materials of invention embodiments are those that maximize the tunability of these properties that can be achieved by predominately non-faradaic electrochemical charge injection. Optional and preferred materials include those providing (1) a low concentration of charge carriers (electrons or holes) at the Fermi level for the uncharged state and (2) a strong dependence of Fermi energy on the amount of charge injection. This strong dependence of Fermi energy on charge injection is typically characteristic of the singularities in density of states found for low dimensional conductors. Hence, 1-D materials (like nanofibers and conjugated polymers like polythiophene) and 2-D layered materials (like cuprates of chalcogenides) are included in optional and preferred compositions. However, materials that can be intercalated (and thereby charge-injected faradaically) are optionally and preferably charged predominately non-faradaically. This can be done by either choosing the potential used for charge injection to avoid proximity to the potentials where faradaic redox reactions occur, or by employing anions and cations that have unsuitable size for intercalation under the kinetic conditions used for charge injection. For example, bundled single-wall carbon nanotubes can be intercalated if the applied potential is either too high or too low (L. Kavan *et al.*, Chem. Phys. Lett. **328**, 363 (2000) and Kavan *et al.*, J. Phys. Chem. B **105**, 10764 (2001)). This intercalation can be avoided by suitably choosing the potential range so that

intercalation does not occur or by using ions in the electrolyte which are too large for facile intercalation.

Materials used for electronic conductivity tuning by non-faradaic electrochemical charge injection are optionally and preferably semiconductors when the goal is to

5 provide the maximum dynamic range of tunability. Materials having singularities in density of states near the Fermi level are optional and especially preferred as materials having tunable electronic conductivity. These include the various well known nanofibers like single-wall and multi-wall carbon nanotube fibers.

The non-faradaically induced increase in electrical conductivity of essentially

10 electrolyte free materials can be usefully employed for making materials that combine high electrical conductivity with high optical transparency. These transparent conducting electrodes are of major applications importance for such applications as liquid crystal displays, light emitting displays (both organic and inorganic), solar cells, switchable transparency windows, solar cells, microlasers, optical modulators, and optical

15 polarizers. Inorganic electrodes like ITO (indium tin oxide) degrade on bending and require costly vacuum based deposition methods. The embodiments of this part of the invention combines our discovery of processes for dramatically enhancing the electrical conductivity of nanostructured carbon nanotubes with prior-art discoveries related to the application of uncharged nanostructured materials for making transparent conductors.

20 The improvement that we bring is to increase the level of electrical conductivity that can be obtained, while still maintaining the desired degree of optical transparency. For example, we demonstrate invention embodiments in which we increase the electrical conductivity of single-wall carbon nanotubes by over an order of magnitude, and retain much or this conductivity enhancement when the electrolyte is removed. The prior art

25 has shown that these nanotubes can also provide reasonably high electrical conductivity, combined with high transparency – our improvement is to increase the achieved electrical conductivity without degrading transparency. In the prior art (International patent number WO 2004/009884 A1 and PCT/US2003/022662 by A. Rinzler and Z. Chen on "Transparent Electrodes from Single wall carbon nanotubes")

30 methods for making electronically conducting, transparent SWNT-containing sheets are

described. The described process enables the achievement of percolation between SWNTs in uniform coatings or films. The achieved sheet resistance is in the range of 200 ohm/sq for an optical transmission of 30%, which can be decreased to 50 ohm/sq for very thin films less than a hundred nanometers thick). However, the sheet resistance should be less than 10 ohm/sq for applications in light emitting displays, solar cells, and other current dependent devices, which can not be achieved by the prior art for carbon nanotubes. The non-faradaic charge injection process of the present invention can accomplish this goal of dramatically reducing electrical resistance, while maintaining optical transparency.

Carbon nanotubes that are non-faradaically injected and largely electrolyte free are optional and especially preferred for invention embodiments directed to highly conducting, optically transparent conductors. These conductors are optionally and preferably in the form of sheet composites or sheet coatings. Also the carbon nanotubes are optionally and preferably single-wall nanotubes (more optionally and preferably either unbundled or having a small bundle diameter). These single-wall carbon nanotubes are optionally and preferably hole injected, since we find that hole-injected carbon nanotubes provide much more stable electrical conductivity enhancements than do electron injected carbon nanotubes. In order to insure long lifetimes for these non-faradaically hole-injected carbon nanotubes, it is generally important to use binder materials that do not contain electron donating impurities have redox potentials that enable reaction with the holes on the nanotubes. To insure that this is the case, any binder composition should have sufficiently high ionization potential that electron transfer does not occur to the hole- injected nanotubes. Many conventional polymers, like polyethylene and polypropylene have this desired characteristic. Conventional methods can be used to treat binder compositions so as to remove trace reactive electron donor impurities that might react with the holes in the hole-injected carbon nanotubes.

The work function of electrode materials generally is very important for applications for either hole or electron injection in organic light emitting displays and for charge carrier collection for solar cells, as well as for related devices. The non-faradaic

charge injection of invention processes provides Fermi level and work function shifts that can be used to optimize this charge injection. The prior art work on multi-wall carbon nanotubes (M. Kruger, et *al.*, Applied Physics Letters **78**, 1291 (2001), and Ch. Schonenberger, ArXiv: cond-mat/0106501, V3, 4 Jan 2002) has shown that the Fermi level increases by up to 0.3-0.5 eV upon electron injection, and decreases by up to 1 eV for hole injection, which will provide corresponding charges in the work function. These prior-art results are from electrochemical charge injection in liquid electrolyte. The enabling improvement of our invention embodiments is that we show that the typically required charge injection can be retained in the absence of contacting electrolyte – either solid or liquid state.

The electron-injected electrolyte-free nanotubes (with decreased work function) are optionally and preferably used as electron-injecting electrodes for such devices as OLEDs. On the other hand, the hole-injected electrolyte-free nanotubes (with increase work function) are optionally and preferably used as hole-injecting electrodes. These hole-injected nanotube electrodes can be used to replace ITO, since they also have large achievable work function and can be used as an effective hole injector for OLEDs.

These device applications of hole-injected and electron-injected electrolyte-free nanostructured materials as charge-injecting electrodes optionally and most preferably utilizes device configurations in which an electrochemical potential is applied to the nanostructured material during device operation. This preference is particularly strong for the electron-injected nanostructured electrodes because charge can only be stabilized on these electron-injected electrodes in an inert environment, and even oxygen exposure can cause degradation if the degree of electron injection is high. On the other hand, hole-injected nanostructured electrodes can easily function without the need for either a continuously-applied or intermittently-applied electrochemical potential to refresh charge injection. Hence, these hole-injected nanotubes can be dispersed in a suitable unreactive binder and used as electrodes for devices, without any need for electrochemical charging after the initial charge injection. Transparent carbon nanotube fiber composites have already been used as replacements for low work function Al or Ag electrodes for plastic donor-acceptor solar cells ("Organic Photovoltaics" Eds. C.

Brabec, V. Dyakonov, J. Parisi and N.S. Sariciftci, Springer Series in Materials Science
Vol. 60, 2003). These nanotubes were not charge injected. The ability provided by the
present invention embodiments is to electrochemically tune the work function of the
nanotubes for this application, without compromising desired performance by the need
5   of the prior art for either dopant intercalation or an imbibed electrolyte.

The processes of invention embodiments can be used for changing the
properties of largely electrolyte-free nanostructured superconductors by substantially
non-faradaic electrochemical charge injection. High temperature superconductors are
optional and most preferred, such as members of the YBCO family. The most preferred
10   compositions include, for example, $LaSrCuO_2$, $YBa_2Cu_3O_{7-x}$, $GdBa_2Cu_3O_{7-x}$,
$BiSr_2CaCu_2O_{8+x}$, and related cuprates. The compositional parameter x is most
especially preferred to be in the range 0.4 to 0.5 for $YBa_2Cu_3O_{7-x}$. Further guidance for
the superconductor compositions that are most suitable for electrochemical non-
faradaic charge injection of invention embodiments can be found in C.L .Lin, et. al.,
15   Applied Physics Letters **71**, 3284 (1997). Although these authors use short lived photo
charge injection to modify the superconducting properties, we find that those
compositions that undergo the greatest changes in superconducting properties upon
photo-injection will also undergo the greatest changes when using the non-faradaic
electrochemical charge invention of the present invention embodiments.

20   These superconducting oxides have low electron density at the Fermi, so non-
faradaically injected charge carriers will significantly change their properties. While the
prior art has used charge injection to modify the T_c of superconductors, this prior-art
work has not used predominately non-faradaic electrochemical charging of a porous
superconductor having a high gravimetric surface area. See, for example, X.X. Xi et.al.
25   in Applied Physics Letters **59** 3470 (1991), who use non-electrochemical process for
switching the superconducting transition temperature of films of $YBa_2Cu_3O_{7-x}$ over 2 K
range. The achieved resistance modulation in the normal state can be as much as 20%
in normal state and 1500% near T_c. Unlike the switching of superconducting properties
in the present invention embodiments the T_c switching observed by Xi *et al.* is not

practically useable for a macroscopic bulk superconducting material and in unstable over the long term if connection to an electrical power source is not maintained.

The non-faradaic charge injection of invention embodiment can be used for tuning superconductors for electronic transport and for electromagnetic wave shielding and propagation for ultraviolet, visible, infrared, radio frequency, and microwave frequencies. One optional and preferred application is as superconducting elements for active filtering, attenuation, phase shifting, and inter-line coupling for microwave electronic transmission lines (such as microstrip line, strip line and co-planar wave guides). Methods for using superconductors for microwave lines and modulated waveguides are well known in the art for the microwave and radio frequency bands, and this technology can be used for application of our non-faradaically charge- injected superconductors. Superconductors of the preferred embodiments may also be used with photonic crystal arrays involving superconducting and semiconducting elements to provide switching of photonic crystal properties in the optional and preferred EM wavelength bands, such as modulation of either the photonic band gap or the width and cut-off frequency of metallicity gap. Other major applications for materials made by processes of invention embodiments are as superconducting transmission lines, and magnets.

Another type of materials which are highly sensitive to EFI (electrolyte free ionic) gate double layer charge injection are the **perovskite manganites** with the general formula $R_{1-x} A_x MnO_3$, with R = trivalent rare earth element and A = divalent alkali earth element. This manganates are extremely interesting for various device applications due to insulator to metal transition (IMT) which is characterized by transformation from the insulating antiferromagnetic (AF) state with localized charge ordering (CO) to a metallic Ferromagnetic (FM) state in which the resistivity is changed by several orders of magnitude. Since this IMT transition is most easily triggered by external magnetic field, at certain doping level x=0.3-0.5, the observed "colossal magnetoresistance" (A.J. Millis, Nature, 392(1998) 147) has been qualitatively explained in terms of double-exchange (DE) effect. This is for example the case in Pr1-xCaxMnO3, in which magnetic field drives a transition into ferromagnetic highly conductive state if the

perovskite is hole doped (Y. Tomioka, et.al., Phys.Rev.B **53** (1996) R1689.) The technical merit of such an IMT ransition is determined by both the controllability and the speed of the transition. It has been also shown that a subtle balance between the AF insulating CO state and magnetic, metallic state can be shifted by application of other external perturbations, like electric field (A.Asamitsu et.al., Nature **388** (1997) 50) , or high pressure (Y.Morimoto, et.al., Phys.Rev.B **55**, (1997) 7549), or exposure to X-rays (V.Kiryukhin, et.al., Nature **386** (1997) 813) or even photoinduced transition by visible light (K.Miyano, et.al., Phys.Rev.Lett. **78** (1997) 4257 and M. Fiebig, et.al., Science **280** (1998) 1925).

We describe as one application of present invention the prototype of a device in which the IMT and CMR can be triggered by EFI-gate charge injection into nanostrutured perovskites, similar to switching caused by applied voltage (or similar effects), that has been observed already in many manganites and can find many exciting applications in microelectronics and nanoelectronics, including high density nonvolatile memory (see for example most recent report S.Q. Liu, et.al., Appl.Phys.Lett., **76** (2000) 2749 or J.Sakai et.al., J.Appl.Phys. **90** (2001) 1410.

An electrolyte free ionic (EFI-)gated perovskite switch that provides the switching of magnetic state from AF to FM with colossal magnetoresistance can be conveniently constructed by using the high-surface-area nanostructured perovskite (R $_{1-x}$ A$_x$ MnO$_3$) mesh, where optional and most preferable R = La, Pr, Nd, Sm, etc, and A = Ba, Ca, Sr) as a CMR active electrode. One method for the fabrication of this high-surface-area mesh electrode is described in already in the mentioned patent of Zakhidov *et al.* This method comprises self-assembling SiO$_2$ spheres as an opal type lattice. These spheres optionally and preferably have a sphere diameter of from about 10 nm to about 300 nm, and are preferably nearly monodispersed in sphere diameter. The spheres are optionally and preferably sintered by thermal annealing to provide a intersphere spacing that is smaller than the sphere diameter. This sintering process enables the extraction of the silica spheres after the infiltration of u R $_{1-x}$ A$_x$ MnO$_3$ by electroplating, CVD or when possible by high pressure to the melt (if such a melt exist), and the subsequent solidification of this perovskite in the void space of the opal. This extraction process is

then conveniently accomplished by immersion of the bismuth-infiltrated silica structure into aqueous hydrofluoric acid solution (in such a ay, that perovskite is not decomposed), so that the silica spheres are dissolved. A plate electrode comprising a high-surface-area wire mesh of results R $_{1-x}$ A$_x$ MnO$_3$ from this easily conducted process

5   if the original silica opal is plate shaped, or if the infiltrated opal is cut into a plate shape after the infiltration process. Another methods to make highly porous perovskites are described above, so that the high-surface-area can be charged by double-layer supercapacitance of the EFI gate of the present invention.

     The solid electrolytes, which can be used for this invention are those, that have

10   been already described for cuprates above in the present patent.

     EFI-gated colossal magnetoresistance switches or memory cells of certain of the preferred embodiments can also be used as resistivity switches that are similar in operation to field effect transistors, but with larger changes of the source to drain current. For example, the R $_{1-x}$ A$_x$ MnO$_3$ inverted opal structures comprising high-

15   surface-area electrodes separated by a solid-state electrolyte can be arranged into an array, similar to array of FET transistors, used in chips.

     In the "on" position, the switche devices could be partially charged and stay in ferromagnetic -FM low resistive state, so that S-D current is very high, controlled by very low voltage at EFI-gate. In the opposite charging state (the "off" position), the

20   switch is turned in to the AF state with localized charges ordering (CO) with high resistance of S-D channel. There is a major need for such electrically controlled CMR switches, controlled by voltage for improving the effective efficiencies of spintronic devices.

     EFI gated CMR switches of certain of the preferred embodiments can be used

25   also broader applications: for the control of the electromagnetic wave propagation for ultraviolet, visible, infrared, radio frequency, and microwave frequency regions, since modulation of electrical conductivity at IMT also changes significantly the refractive index, dielectric constant, absorption, and optical reflectivity – all of which result from double-layer charge injection of the present invention.

It should be noted, that the subtle balance of the AF and FM states of perovskites R $_{1-x}$ A$_x$ MnO$_3$. at appropriate doping level $0.3 < x < 0.5$, can be shifted easily by the EFI gate charging, and this shift will cause the high sensitivity of the IMT to the external fields. Since charge and spin are very strongly coupled in perovskites, as
5   well as charge is coupled to orbital and lattice degrees of freedom, the EFI-gated perovskite electrode should be triggered into the CMR state by applying an external magnetic field in a different way, compared to uncharged electrode. This opens a way to lower or increase the threshold magnetic field by the EFI gate.

The use of EFI gated perovskites as the channel of spintronic devices, between
10   magnetic source and drain will be one of most interesting applications.
Similarly the photoinduced switching to CMR state can be fine tuned by EFI-gate charging, and this phenomena can be used in various types of optical switches, photosensors, light limiters, and other optoelectronic devices, which also can be sensitive to magnetic field.

15   Devices of invention embodiments generally include at least three elements: a working electrode, a counter electrode and a possibly multi-component electrolyte material that helps provide an ion conducting path between the working and counter electrodes. Electrochemical charge injection in an electrolyte-free electrode component is accomplished by applying a voltage between at least two electrodes that are both in
20   partial contact with an electrolyte, where an uninterrupted path for ionic transport exists between these two electrodes.

Figure 9 schematically illustrates means used in invention embodiments for injecting charge into a high-surface-area electrode that is only partially contacted with electrolyte. The charged state is pictured, where 900 is the electrode with positive
25   injected electronic charge (electrostatically balanced by pictured anions that are in close proximity, symbolized by the white spheres) and 910 is the counter electrode with negative injected charge (electrostatically balanced with pictured cations, symbolized by black spheres). The nanostructured electrode materials for both 900 and 910 are single-wall nanotubes, although virtually any type of nanostructured conductor can be
30   used (as long as this conductor does not undergo degradative intercalation in the

potential range of device operation). Material selection depends upon the device type and performance needs. Component 920 is an electrolyte, which only partially contacts the electrodes 900 and 910. The variable voltage power source and associated leads that electrically connect to the two nanotube electrodes of 900 and 910 is 930. An applied potential from a power source 930 injects charge of opposite sign in the two pictured single-wall carbon nanotube electrodes 900 and 910. The needed counter ions diffuse along the nanotube surfaces to enable this electronic charge injection. Reversing the direction of current flow, by changing the applied potential, causes the ions to diffuse from the nanotube surfaces back to the electrolyte 920.

For comparison with the electrochemical semiconductor device in Figure 11 of the present invention, Figure 10 illustrates a prior-art electrochemical semiconductor transistor device. The illustrated prior-art device of Figure 10 is referred to in the literature (M. Krüger, Applied Physics Letters **78**, 1291-1293 (2001)) as being a "liquid-ion gated" device. The device is separated from the substrate 1000 by an insulating layer 1010 (typically SO_2). The device channel and an electrochemical electrode (1020) is a semiconducting carbon nanotube, which is contacted by metal source and drain electrodes (1070 and 1080, respectively). The device is liquid-ion gated by using the variable potential source 1060 and associated wiring to apply a potential between the micropipette (1040) enclosed Pt wire electrode (1050) and the carbon nanotube electrode (1020), which is analogous to the channel of a conventional field effect transistor. The electrolyte (1030) covers both the nanotube channel electrode and the Pt wire counter-electrode (1050). The device operates by using the power or signal source of 1060 to electrochemically inject charge into the nanotube electrode/channel (1020). This injected charge changes the electrical conductivity of the nanotube channel (1020), thereby varying the current that flows through the channel in response to a voltage difference applied between source electrode 1070 and drain electrode 1080. This device is called a liquid-ion gated FET, since the nanotube channel (1020) is immersed in a liquid electrolyte and the ions in this electrolyte are needed for the charge injection (i.e., gating) process. This or other prior art does not recognize that electrochemical double-layer charge injection can result for electrode regions that are

not in electrolyte, which is the reason for the illustrated complete immersion of the nanotube in the electrolyte. This immersion of the channel (1020) in a liquid electrolyte is clearly problematic for ordinary transistor applications. The device of Figure 10 could be used as a Chem-FET (chemical sensor based on a FET) for detecting materials

5   dissolved in the electrolyte, by using the effect of these materials on double-layer charge injection. However, if the material to be detected is a gas, this material must first dissolve in the electrolyte – which decreases device response rate and sensitivity.

Figure 11 schematically illustrates an electrochemical transistor of the present invention embodiments that is not liquid-ion gated. We call this an Electrolyte Bare Ion

10   Gated device (EBIG device), since the electrolyte is not deposited to completely overlap the device channel, and the region of the device that is bare of electrolyte facilitates device function. The device is built over a trench (1180) in an insulating substrate (1170). There are two device channels, and neither of these channels is in contact with a liquid electrolyte. More generally important, the component of each channel that

15   largely determines gate resistivity is not surrounded by either a liquid electrolyte or a solid electrolyte. There are two source and drain electrodes (1100 and 1110, respectively) for the first leg of the device and two source and drain channels (1120 and 1130, respectively) for the second leg of the device. Likewise there are two semiconductor channels. The channel for the first leg of the device (1140) and the

20   channel for the second leg of the device (1150) can be, for example, nanofibers (such as carbon SWNTs). A solid-state electrolyte (1160) lays over part of the source and drain electrodes and the channel for each leg of the device.

Device operation is as follows: Application of a voltage difference between electrode 1100 and 1120 (or gate electrode 1100 and 1130) causes predominately non-

25   faradaic charge injection of opposite sign in channels 1140 and 1150. This charge injection is enabled by the surface diffusion of cations to electrostatically compensate electrons motion for the more negatively charged channel and by the surface diffusion of anions to electrostatically compensate hole motion for the more positively charged channel. This charge injection in the active channel lengths (predominately the channel

30   lengths that are suspended over trench 1180). This charge injection changes in a

controllable way the electrical conductivity of the channels, which is indicated by a change in the current passing between electrodes 1100 and 1110 in response to an applied potential between these source and drain electrodes (and between 1120 and 1130 in response to a applied potential between these electrodes).

5　　　The device of Figure 11 (and a related device of Figure 12) can be operated as a replacement for a field-effect transistor, or in such applications as information storage or gas sensing. Because of the dual leg nature of the Figure 11 device, this device provides two transistor elements, two information storage elements, and two sensors that are controlled in a correlated manner.

10　　　When used as a chemical sensor for gas state species, a gas phase species interacts with the channel in a way dependent on the charged state of this channel, to thereby provide a change in the resistivity of this channel. Importantly, this and related devices of invention embodiments can be used to do something that has heretofore been impossible – to do the equivalent of cyclic voltametry for substances that are

15　　directly delivered to the device channel (or channels) in gaseous state. This unprecedented device capability results from the fact that materials in the environment of the channel will undergo redox reaction with charges on the channel.

　　　Like for ordinary liquid state cyclic voltametry, the existence and rate of such reaction for a particular species in the gaseous state will depend upon the redox

20　　potentials for these species. In standard liquid-state cyclic voltametry, one scans electrode potential at a constant rate and then plots the resulting inter-electrode current flow versus the applied potential. For the device of Figure 11 and devices of related invention embodiments, additional sensor information can be collected that helps uniquely characterize gas phase species. This information is the effect of such gas-

25　　state-delivered species on the channel resistance as a function of channel potential.

　　　The device pictured in Figure 11 does not provide a reference electrode, which is typically used in liquid state cyclic voltametry. Such a reference electrode, or more than one reference electrode, can be usefully incorporated in the device of Figure 11 by including a reference electrode material (such as a platinum wire or a platinum film) in

30　　electrolyte 1160. This reference electrode (or a multiplicity of such reference

electrodes) should not be in electrical contact with other conductive elements of the device. Measurement of the potential of a channel with respect to a reference electrode (which are optionally and preferably located in close proximity) enables placement of channel potentials on an absolute scale, so that the redox potentials of detected gas phase species can be most reliably determined. The two channel materials in Figure 12 need not identical or even comprise a nanofiber. Specifically, the use of film strips for one or more of these channels is also included in preferred invention embodiments. However, these channel materials should optionally and preferably have both semiconducting and highly conducting states and the possibility of transitioning between these states as a result of charge injection. One of these channel materials can optionally also be a material that is predominately charged faradaically in the potential range of device operation, such as a conducting organic polymer or vanadium pentoxide nanostrip fibers (see G. Gu et al., Nature Materials **2**, 316-319 (2003) and provided references for description of the synthesis, properties, and self-assembly of these vanadium pentoxide nano-strip fibers).

Figure 12 schematically illustrates a second electrochemical transistor device of the present invention that does not use liquid-ion gating, which could be used for information storage or gas sensing. Like the device of Figure 11, this is also a EBIG device - but unlike the device of Figure 11 the present device has only one channel. The device is configured over a trench (1270) in an insulating substrate (1260). The operation and benefits of this device are similar to that of the device in Figure 12. A potential applied between gate electrode 1220 and source electrode 1210 controls the amount of charge injection in the channel 1230, which optionally and preferably is a semiconductor when there is no change injection. This charge injection changes the electrical conductivity of the channel, which is measured by applying a voltage between source electrode 1210 and drain electrode 1200 and measuring the resulting current flow through channel 1230. A material 1240 capable of charge injection overlies the gate electrode and is electronically part of this gate electrode. This material can undergo charge injection either predominately non-faradaically or predominately non-faradaically in the gate-source voltage operation range of the device. The solid-state

electrolyte 1280 contacts the material 1240 and the channel material 1230, and provides an ion conducting path between these elements. However, the measured conductivity of the channel is in large part determined by regions of the channel that do not contact the channel, and the charging of this channel is optionally and preferably

5   predominately non-faradaic in the typically utilized operation range of the device.

Is well known in the prior art that faradaic charge injection can profoundly affect the optical properties of material and that these faradaically-changed optical properties can be maintained in the absence of an electrolyte. However, prior-art investigators have not discovered that optical properties changes can result from non-faradaic

10   charge injection that is accomplished without direct contact of an ionically conducting material (such as an electrolyte or electronically intercalated conducting polymer).

The optical device schematically illustrated in Figure 13, which is illustrative of many related devices of the invention embodiments, utilizes our above discoveries. Devices of this and related types of the invention embodiments provide the switching or

15   optical properties of a material region that is not directly contacted with an electrolyte or an intercalated material that provides ion transport. Typical applications of these devices are gas sensors based on surface enhanced Raman (SERS) or fluorescence, infrared camouflage layers, and electronically switchable photonic crystal mirrors.

Figure 13 schematically illustrates an optical gas sensor, based on the surface-

20   enhanced Raman effect, that uses electrochemically controlled charge injection in a metallo-dielectric photonic crystal to optimize sensitivity and species selectivity. The desired device performance enhancement originates from a number of possible elects, including (1) the charge-injection-tuned pickup of gas phase components that are to be sensed and (2) the optimization of the resonant effect of SERS by charge-injection-

25   based tuning of plasma frequency (and therefore the resonance enhancement of the SERS effect). Methods for fabricating such a metallo-dielectric photonic crystal (which optionally and preferably is from a high reflectivity metal like silver) are described, for example, in A. A. Zakhidov *et al.*, U.S. Patent 6,261,469 and U.S. 6,517,762, L. Xu *et al.*, Advanced Materials **15**, 1562-1564 (2003), and L. Xu *et al.*, J. Am. Chem. Soc. **123**,

30   763 (2001).

Element 1300 of Figure 13 is an inverse lattice photonic crystal, which also functions as a working electrochemical electrode. This element is preferably a conducting photonic crystal having a void volume of greater than about 50%. This element is optionally and preferably an inverse lattice photonic crystal that is comprised of a high reflectivity metal like silver. Element 1320 is a solid-state electrolyte that contacts the photonic crystal. The solid-state electrolyte preferably has low electronic conductivity and an ionic conductivity of above 10^{-4} S/cm at room temperature. Element 1310 is a counter electrode to the working electrode 1300, which is also a photonic crystal. This counter electrode can be a one that operates predominately faradaically or predominately non-faradaically. Intercalated conducting polymers that undergo predominately faradaic charging during device operation or very high surface area non-intercalated materials (like nanoporous Pt or nanofibers) are optional and preferred for use as this counter-electrode. This counter electrode element 1310 can optionally be a second photonic crystal that is optionally and preferably predominately charged non-faradaically during device operation. The benefit of using two photonic crystals is that one obtains two materials for SERS sensing (one with negatively injected charge and the other with positively injected charge), which can be simultaneously probed optically during device operation. Element 1330 is a variable voltage or variable current power supply, and associated electrical wires to the working electrode (1340) and the counter electrode (1310). Item 1340 in Figure 13 indicates the input and output of light to the photonic crystal, which need not be in the pictured orthogonal direction to the photonic crystal surface. The electrolyte element 1320 optionally and preferably includes a reference electrode (not shown) for placing measured potentials on an electrochemical scale – so that the degree of charging can be determined from the measured potential of 1300 with respect to this reference electrode, and used to control the degree of charge injection for 1300.

Application of the device of Figure 13 as a SERS based gas sensor is as follows: Applying a potential between the working electrode 1300 and the counter electrode 1310 injects change into the photonic crystal electrode (1300), thereby modifying the adsorption of targeted materials onto the external and internal surfaces of 1300 and

appropriately shifting the frequency of surface plasmons. Different gas components can be selectively detected by measuring the SERS spectra during scanning the degree of charge injection in 1300. Either this device scanning is at a sufficiently slow rate that surface adsorption and desorption can be accomplished at ambient temperature or

5   heating of component 1300 can be used to accelerate these surface absorption and desorption processes. This heating can be accomplished either electrically by resistance heating or by the heating effect of radiation adsorption. Monitoring the SERS spectra during heating and cooling processes is usefully employed for obtaining additional information about the composition of the sensed gas.

10   Like for most of the devices of invention embodiments, the device of Figure 13 can be operated either in a "rocking chair device" mode or in an "electrolyte ion storage" mode, or as a combination thereof. In the rocking chair mode, ions are shuttled between working and counter electrodes during device operation, and the function of the electrolyte (1320) is just to electronically insulate the working and counter

15   electrodes and to enable ionic transport between them. In the electrolyte ion storage mode, the electrolyte stores the ions that are injected into opposite electrodes during device operation (typically anions for one electrode and cations for the opposing electrode for a given change in inter-electrode operation voltage). If there is only one mobile ion in the device system, then the device operation will be by the rocking chair

20   mode, which requires only sufficient electrolyte (1320) to insure that the working electrode (1300) and the counter electrode (1310) are electronically insulated with respect to each other and that these electrodes are intimately contacted by the electrolyte. Although device operation in either of these modes can be usefully employed for this and other devices of invention embodiments, device operation in

25   predominately the rocking chair mode is optional and more preferred. The reason is that operation in strictly a rocking chair device mode requires that at least one of these electrodes is charge injected during device fabrication. Since operation in the electrolyte ion storage mode is optional and more preferred, this means that electrolytes having two types of mobile ions are generally preferred for invention embodiments. An

30   exception to this is provided by fuel cell devices of invention embodiments (based on

either hydrogen or hydrocarbon fuels), where electrolytes providing predominately H^+ ionic conduction are optional and more preferred, because of the need for H^+ ion conduction for these fuel cells and the relatively high electronic conductivities of many H^+ transporting electrolytes.

5   Devices having the basic configuration shown in Figure 13 can also be used to switch other properties of the working electrode of this figure, especially magnetic properties, electrical conductivity, microwave absorption, surface energy, thermal diffusivity and thermal conductivity, thermopower, the existence and characteristics of superconductivity, and even surface friction coefficients. For all of these application

10   modes except switching surface friction and switching surface energy, it is preferred that the working electrode material comprises at least 25% void volume. More preferably, the void volume is at least about 50%, and most preferably this void volume is at least about 75% for the working electrode. Specific compositions optional and preferred for these types of devices are listed elsewhere in this section.

15   Devices of invention embodiments also provide electromechanical actuation and electrochemical tunable chemical actuation. It is well know that charge injection, either faradaic or non-faradaic, can provide electrochemical electromechanical actuation. For examples of such faradaic and non-faradaic actuation, see R.H. Baughman, Synthetic Metals **78**, 339-353 (1996); R. H. Baughman *et al.*, Science **284**, 1340 (1999); R. H.

20   Baughman *et al.*, U.S. 6,555,945; G. Gu *et al.*, Nature Materials **2**, 316-319 (2003); and R.H. Baughman, A.A. Zakhidov, and W.A. de Heer, Science **297**, 787-792 (2002). A problem with prior art technologies of actuation using electrochemically-induced dimensional changes is that an electrolyte must be used, and both solid-state and liquid electrolytes provide disadvantages. First, liquid electrolytes are generally problematic

25   because of the need for electrolyte containment, and on the microscale (for anything other than microfluidic applications) incompatibility with conveniently employable device fabrication methods. Second, while the use of liquid electrolytes can avoid these problems, others appear. Most importantly, the mechanical modulus of the electrolyte acts to constrain the achievable actuation in the best case, and in the worst case (for

30   electrolyte ion storage operation modes) the electrolytes provide dimensional changes

themselves and these electrolyte-induced dimensional changes work in opposition to the dimensional changes of at least one of the actuator devices. Hence, these all-solid-state electrochemical electromechanical actuators have been cantilever devices. These cantilever devices, when based on a porous actuator electrode, contain electrolyte in

5   the volume of this electrode, as well as a separator between the two needed electrodes. Hence, these prior-art all-solid-state electrochemical electromechanical actuator operate by bending, thereby utilizing the mismatch in electrochemically induced dimensional changes of mechanically coupled opposite electrodes. This presents a problem, since such bending actuators do not provide a very efficient way to

10   convert electrical energy to mechanical energy.

This non-faradaic process charge injection process used for actuation is fundamentally different from that for previously known magnetostrictive, electrostrictive, ferroelectric, electrostatic, shape-memory, and faradaic electrochemical processes. Unlike faradaic electrochemical actuators, the non-faradaic actuators of some preferred

15   embodiments do not require dopant intercalation and de-intercalation during the actuator cycle, so they do not suffer from cycle life and cycle rate limitations from such partially irreversible processes.

The mechanical actuators of the present invention embodiments can be run in reverse to convert mechanical energy to electrical energy for mechanical sensor and

20   energy conversion devices. The benefits of using electrode elements that are not in direct contact with the electrolyte is the same as for the above described actuators that are used to convert electrical energy to mechanical energy. For cases in which the working and counter electrodes are identical, the generation of electrical energy requires that mechanical stress be applied differently to these electrodes. Optionally

25   and most preferably, a tensile stress is applied to one electrode while a compressive stress is applied to the other electrode. These electrochemical devices for sensing mechanical stress and strain and for converting mechanical energy to electrical energy generate high currents at low voltages, which provides advantages for some applications over ferroelectric mechanical-to-electrical energy converters, which

30   generate low currents at high voltages. This performance of our electrochemical energy

converters is desirable for minimizing the effect of lead capacitances for remotely located sensors, so that sensor-response amplifiers need not be located down-hole when doing seismology for oil exploration. The ability to operate these energy harvesting devices at low frequencies could be usefully exploited for the conversion of mechanical energy of ocean waves to electrical energy. An array of such devices are optionally and preferably electrically interconnected in series to provide an increased output voltage. In another preferred embodiment, the electrodes of the electrochemical electromechanical energy harvesting device are electrically biased during device operation using an applied voltage. An advantage of such biasing is that the electrical energy generated by mechanical stress can be increased. However, when using such biasing, the stress generated voltage changes should optionally and preferably be electrically isolated from the biasing voltage. Optionally and preferably, this is accomplished by using a capacitor in series with the bias circuit. These devices used to convert mechanical energy to electrical energy optionally and preferably utilize either a uniaxial or biaxial applied stress. Device polarity is optionally and preferably achieved using different materials for opposing electrodes, an applied bias voltage, or the application of differing stresses to the opposing electrodes.

Carbon nanotubes are currently widely studied as an optional and preferred source for electric-field-induced electron emission (so-called cold electron emission). They are already used as a cold cathode for numerous applications, such as Field Emission Displays (FEDs) and x-ray sources. Our invention embodiments enable gate-controlled electrochemical charge injection in carbon nanotubes for the optimization and control of the electronic work function of the carbon nanotubes, and therefore their emission characteristics. When electrons are injected into the nanotubes the work function decreases and when holes are injected the work function increases.

The devices of this invention may comprise more that two current carrying electrodes that can be operated at different voltages. Advantages of using more than two current carrying electrodes are that additional flexibility is achieved with respect to the degree of charge injection in the individual electrodes, which can be useful for optimizing device performance.

In a preferred process of our invention, electrode charging for at least one electrode is predominately non-faradaic, meaning that over 50% of the initially injected charge is injected non-faradaically. It should be emphasized that this definition pertains to the nature of initial charge injection from the electrolyte, since initially non-faradaically injected charge can later transform to charge that is retained faradaically during electrode drying processes. Such is the case if dopant ions that are initially stored in an electrochemical double layer later intercalate into the electrode material. In the non-faradaic process of certain preferred embodiments, the ions from the electrolyte (which compensate the electronic charges injected into the electrodes) are located close to the surface of at least one of these electrode elements. This is in contrast to the faradaic processes where the ions that compensate the injected electronic charges penetrate inside the electrode material and change its structure, usually expanding it. In the more preferred invention embodiments, over 50% of the fraction of the stored charge is stored non-faradaically in the charged material, meaning that at least 50% of this stored charge is associated with ions on or near the surface of the material. In the most preferred invention embodiments, over 75% of the fraction of the stored charge is stored non-faradaically in the charged material, meaning that at least 75% of this stored charge is associated with ions on or near the surface of the material. Because of this location of charge on material surfaces in the non-faradaic process of the preferred embodiments, ions from the electrolyte need not penetrate the electrode material and need not cause phase changes within the electrode material. This preference for non-faradaic charge injection is generally most important for device applications where the charge injected electrode material must be repeatedly charged and discharged during device operation, since non-faradiac charge injection generally provides longer device cycle life than does faradaic charge injection. It should be recognized that charge injection processes can be non-faradaic over one potential range, and then become faradaic when this potential range is extended. Consequently the definitions of predominately non-faradaic and predominately non-faradaic indirectly signify the potential range used for hole or electron charging. A device is called a predominately non-faradaic as long as there is a device operation range where a useful

device response can be obtained from predominately non-faradaic charging of at least one electrode.

The achievement of very high electrode capacitances requires the use of nanostructured materials that have small sizes in at least one dimension, and such small dimensions can affect the properties of the nanostructured material in both charge-injected and non-charge-injected states. Consequently, the use of materials with larger dimensions (sheet thicknesses, fiber diameters, or particle sizes) can in some cases be preferred (with a corresponding decrease in preferred electrode capacitances) – especially for the tuning of highly-scale-sensitive properties, such as ferromagnetism.

The case where only the working electrode operates predominately non-faradaically is also included in invention embodiments. Devices in which ions predominately insert on the internal and external surface of one electrode and in the material volume of the second electrode are included here. This can be a preferred embodiment in the case where cycle life limitations are not problematic for the desired application mode or where the potentially higher charge storage densities of faradiac processes provide needed benefits of reduced device size or weight. However, predominately non-faradaic operation of both electrodes is optional and preferred when very long device cycle lifetimes are needed, when charge-injection modified properties of both electrodes are utilized, or when dopant intercalation and associated structural changes degrade needed properties.

The device types of the preferred embodiment optionally and preferably have at least one electrode (optionally and preferably the working electrode) that has high gravimetric surface area, since this high surface area is typically required to obtain high degrees of double-layer (non-faradaic) charge injection. In fact, material selection to provide either predominately non-faradaic or predominately faradaic performance is made according to either surface area measurements or structural results (from typically scanning electron microscopy, SEM, electron transmission microscopy, TEM, or atomic probe microscopies). The gravimetric surface area is conveniently taken as the surface area measured in nitrogen gas by the standard Brunauer-Emmett-Teller (BET) method. The gravimetric surface area of the working electrode is preferably

above about 1 m^2/gm, more preferably above about 10 m^2/gm, and most preferably above about 100 m^2/gm. In some instances where the electrodes must be repeatedly charged and discharged during device operation and long cycle life is needed, the surface area of both working and counter electrodes is preferably above 1 m^2/gm, more

5   preferably above about 10 m^2/gm, and most preferably above about 100 m^2/gm.

It is optional and preferred for some device embodiments that either the working electrode or both working and counter electrodes comprise a mixture of electronically conductive materials that serve as electrode components. Most preferred here is the case wherein this mixture of materials includes materials that are non-faradaically

10   charged and faradaically charged. Further details on preferred configurations for these two components will be later provided in sections where we describe methods for making devices and for increasing the stability of charge-injected states.

The working and counter-electrodes can be made of either the same or different materials. Optional and preferred examples of electrode materials include high surface

15   area metallic compositions obtained by the degenerate doping of semiconductors (such as Si, Ge, mixtures of Si and Ge, and GaAs), (b) conducting forms of conjugated organic polymers (such as polyacetylene, poly(p-phenylene), or poly(p-phenylene vinylene) and copolymers thereof), (c) carbonaceous materials obtained by the pyrolysis and surface area enhancement of polymers, (d) graphite, carbon nanotubes,

20   and less ordered forms of carbon formed by pyrolysis, (e) elemental metals and alloys of these metals, and (f) electrically conducting metal oxides and metal sulfides.

Organic conducting polymers are among the more preferred compositions for use as predominately faradaic electrodes. Very high surface area conducting polymers are included in preferred compositions for predominately non-faradaic electrodes.

25   Various methods can be used to obtain conducting polymer electrodes having high surface areas. For example, known methods can be used for the electrostatic spinning of conducting polymers into nanometer diameter fibers. For these conducting polymers the predominately non-faradaic behavior is obtained as a result of this high surface area and operation of the electrodes in potential ranges where the major faradaic

30   process do not substantially occur. Especially preferred organic conducting polymers

are those with planar or nearly planar backbones, such as poly(p-phenylene), poly(p-phenylene vinylene), and polyacetylene. Other preferred conducting polymers are various conducting polypyrroles, polyanilines, polyalkylthiophenes, and polyarylvinylenes. The synthesis of conducting polymers suitable for the preferred embodiments is well known, and is described, for example, in the Handbook of Conducting Polymers, Second Edition, Eds. T. A. Skotheim et al. (Marcel Dekker, New York, 1998).

Forms of elemental carbon, especially carbon nanofibers or graphite are included in optional and preferred compositions as one or more electrodes for invention embodiments. Like for the case of conducting polymers most of these carbon compositions can be used as either predominately non-faradaic or predominately faradaic electrodes, depending upon the gravimetric surface area of the form of carbon and the potential of device operation. For use as a non-faradaic electrode or non-faradaic electrode component, graphite is most especially preferred to be in the form of largely exfoliated graphite. Optional and preferred carbon fibers include multi-wall nanotubes (which consist of concentric graphite sheets), single-wall nanotubes (which exhibit a single cylindrical graphite sheet), carbon fiber scrolls (a spirally wound graphite sheet), and carbon fibers with radial alignment (in which graphite planes extend radially about the fiber direction). Since multi-wall carbon nanotubes, single-wall carbon nanotubes (SWNTs), and carbon nanotube scrolls have hollow interiors, these hollow materials can optionally be filled by insulating, semiconducting, or metallic compositions by known methods, so as to thereby modify charge injection characteristics. In order to maximize surface area for predominately non-faradaic charging, the number-average diameter of single-wall and multi-wall carbon nanotubes used as predominately non-faradaic electrodes is preferably below about 10 nm. The term number-average diameter means the ordinary average of the diameters of the nanotubes, without any special weighting according to the size of the diameter.

Single-wall carbon nanotubes (SWNTs) are optional and especially preferred for use as electrodes. The dual laser method, the chemical vapor deposition (CVD) method, and the carbon-arc method are optional and preferred methods for making the

carbon nanotubes, especially single-wall carbon nanotubes, and these methods are well known in the literature (R. G. Ding *et al.*, Journal of Nanoscience and Nanotechnology 1, 7 (2001)). Carbon single-wall nanotubes can have armchair, zigzag, or chiral arrangements of carbon atoms. These nanotubes are differentiated in that the armchair nanotubes have a circumference consisting of para-connected hexagonal rings (like found in poly(p-phenylene)), the zigzag nanotubes have a circumference that consists of linearly side-connected hexagonal rings (like found in linear acenes), and the chiral nanotubes differ from the armchair and zigzag nanotubes in that they have a sense of handedness. The geometry of carbon nanotubes is specified using conventional nomenclature using the indices (n, m). Depending on the appearance of a belt of carbon bonds around the nanotube diameter, the nanotube is the armchair (n=m), zig-zag (n or m=0), or chiral (any other n and m) variety. All armchair SWNTs are metals; those with $n-m = 3\,k$, where k is a nonzero integer, are semiconductors with a tiny bandgap; and all others are semiconductors with a bandgap that inversely depends on the nanotube diameter. Since methods are available for selecting carbon nanotubes according to conductivity type, we can optimize the choice of nanotubes for particular applications. The optional and preferred SWNT type depends upon the device or materials application. Metallic nanotubes are optional and preferred for applications where maximum conductivity is desired, such as for transparent conductors or as counter electrodes where rapid response rate is desired. On the other hand, semiconducting nanotubes are desired for the channel material for semiconductor devices of the present invention.

Aerogels, and especially carbon aerogels and aerogels based on conducting organic polymers, are included in the list of optional and preferred actuator electrode materials. Resorcinal-formaldehyde derived carbon aerogels are especially preferred carbon aerogels. These carbon aerogels can be conveniently produced using the sol gel method, supercritical drying using liquid CO_2, and pyrolysis in nitrogen at about 1000° C. The synthesis of these carbon aerogels is described by Salinger *et al.* in Journal of Non-Crystalline Solids **225**, 81 (1998).

Various methods are well known in the literature for assembling nanostructured fibers and particles into forms well suited for the practice of the present invention. For example sheet shaped electrodes of single-wall nanotubes can be conveniently formed by filtering an aqueous suspension of such purified carbon tubes through poly(tetrafluoroethylene) filter paper, as described by Lui *et al.* in Science **280**, 1253 (1998). Peeling the resulting paper-like sheet from the filter results in a freestanding sheet of carbon nanotube bundles. This sheet, which can conveniently range in thickness from 0.1-100 microns, possesses mechanical strength, which is derived from the micro-scale entanglement of the nanotube bundles. In order to increase the mechanical properties of these sheets for the applications, it is preferable for the nanotube sheets to be annealed at a temperature of at least 400° C for 0.5 hour or longer prior to use. More preferably, these nanotube sheets should be annealed at a temperature of at least 1000° C for 0.5 hour or longer in either an inert atmosphere or a hydrogen-containing atmosphere. In order to preserve the nanotube structure, this anneal temperature is preferably below 2000° C. Alternatively, carbon nanotubes can be deposited on a surface by deposition from a dispersion of nanotubes in a liquid, such as dichloroethane or water, which contains a surfactant (such as triton X-100 from Aldrich, Milwaukee, WI). Well known and widely practiced micro-lithographic techniques can be used to obtain patterned depositions and to anchor the nanotubes on the substrate. For example, either one or both ends of an individual tube can be pinned to the substrate by an over-layer, so that a controllable length of the nanotube is left uncovered. A useful solution to the problem of firmly mechanically and electrically contacting individual single-wall nanotubes or single-wall nanotubes bundles (without constraining movement at locations away from contact points) has been described by D. A. Walters *et al.* in Applied Physics Letters 74, 3803-3805 (1999). Using micro-lithographic techniques, these authors demonstrated that single-wall nanotubes could be rigidly attached on opposite ends (both electrically and mechanically), so that they are suspended over a microscopic trench.

Another optional and preferred way to make the high-surface-area materials used in invention embodiments is by templating a self-assembled structure that has

high surface area. For example, a periodic template crystal (called an opal) can be obtained by the sedimentation of spheres that are substantially monodispersed in diameter. These spheres optionally and preferably have an average sphere diameter of between 500 nm and 10 nm. In most preferred cases, these spheres are from either (a) an inorganic oxide, such as SiO_2, which can be removed by chemical processes such as exposure to aqueous acid or base, or (b) an organic polymer that can be removed by pyrolysis, chemical reaction, or dissolution. The template crystal, after an optional and preferred sintering process to provide inter-sphere necks, is infiltrated with either the actuator material or a material that can be converted to the actuator material. This sintering process in described by Zakhidov *et al.* in Science 282, 897 (1998) and U.S. Patent 6,261,469 and U.S. 6,517,762. Thereafter, the template material is removed to provide an inverse lattice, which is a structural replica of the original template crystal. As an example, Zakhidov *et al.* (Science 282, 897 (1998)) used plasma-enhanced CVD to make a very high surface area graphitic carbon. Millimeter thick opal plates based on monodispersed SiO_2 spheres were infiltrated with carbon from a hydrogen/methane plasma created by microwave excitation. Extraction of the SiO_2 spheres from the carbon infiltrated opal (using aqueous HF) resulted in a very high surface area, nanoporous foam in which carbon layers as thin as 40 Å make the internal surface of the foam. As another optional and preferred method for fabrication conducting sphere arrays having high surface area for use as nanostructured electrodes, conducting spheres that are nearly monodispersed in diameter can be directly assembled from sphere dispersions using conventional methods. These spheres are preferably less than about 200 nm in average diameter, more preferably less than 100 nm in average sphere diameter, and most preferable less than 50 nm in average sphere diameter.

The relative and absolute sizes of working and counter-electrodes are important for determining optimal device design. Consider first the case where both working and counter electrodes operate predominately non-faradaically. In order to obtain rapid switching of the properties of the working electrode (without the necessity of faradaic processes in the electrolyte that can degrade cycle life) the total surface area of the counter electrode should preferably be at least twice as large as large as the working

electrode. If a more rapid device response is required, it is more preferred that the total surface area of the counter electrode is at least about ten times larger than that of the working electrode. For microdevices having extremely fast switching rates, it is most preferred that the total surface area of the counter electrode is at least about a hundred times larger than that of the working electrode. The preferred conditions for high rate switching of the properties of the properties of the working electrode can also be expressed in terms of electrode capacitance, where the ratio of counter-electrode to working-electrode capacitances is preferably at least about 2, more preferably at least about ten times, and most preferably (for certain high rate devices) about at least a hundred times larger than that of the working electrode.

In addition to optimizing rate performance, these preferred, more preferred, and most preferred relative surface areas and relative electrode capacitances determine the fraction of total applied inter-electrode potential that is applied across each individual electrode. Since the total potential that can be applied is typically determined by the stability of the electrolyte, the selection of increasingly large values for these ratios is also desirable for increasing the fraction of the applied potential that is applied across the working electrode, and therefore increasing the amount of charge injection in this electrode and the corresponding degree of properties change for this electrode. On the other hand, the selection of capacitance and surface areas close to unity can be desirable if substantial properties switching is needed for both electrodes or if there is a need to minimize device size or weight. Device response rate decreases with increasing size and increasing thickness electrodes, and the lowest capacitance electrode typically determines response rate. Hence, for applications were high charge and discharge rates are needed, the thickness of the lowest capacity electrode should be preferably below about five millimeters (5000 microns and 10^7 nm), more preferably below about 1000 microns, most preferably below about 100 microns, and most especially preferably below 50 microns. However, it should be understood from the present teachings that much thinner electrodes can be desirably used when very fast rate response is not a performance issue and much thinner electrodes are optionally and

preferably used in microscopic devices where very small sizes and very high charge/discharge rates are required.

With further regard to the rate of device response, the rate response (as a fraction of the maximum achievable response) increases with increasing values of $(R_S C_S)^{-1}$, where R_S is the effective resistance of the electrochemical system and C_S is the effective capacitance of this system. Key contributions to R_S can come from the resistivities of the working and counter electrodes and the resistivity of the electrolyte for ionic conduction. Consequently, it is optional and preferred that the device contains at least one electrode having an electronic conductivity at room temperature that is above 1 S/cm. More preferably at least one electrode has an electronic conductivity at room temperature that is above 100 S/cm. Most preferably at least one electrode has an electronic conductivity at room temperature that is above 1000 S/cm. Most especially preferred, the device contains at least two electrodes that each has an electronic conductivity at room temperature that is above 1000 S/cm. In general the electrical conductivities of nanotube assemblies will be anisotropic and depend upon the degree of charge injection. In such case the conductivities referred to above correspond to the highest conductivity direction of the conducting material in the most conducting state obtained by charge injection.

From a viewpoint of having fast charge and discharge rates, the ionic conductivity of the electrolyte is preferably above 10^{-4} S/cm, more preferably above about 10^{-3} S/cm, and most preferably above about 10^{-1} S/cm. In addition, device response rates are enhanced for the more poorly conducting electrolytes by minimizing the average thickness of electrolyte that separates the at least two typically required device electrodes. The maximum electrolyte thickness that separates the two typically required electrodes is preferably less than 1 millimeter when these electrolytes are solid-state inorganic or organic electrolytes. More preferably this average electrolyte thickness is less than 0.1 millimeters for solid-state electrolytes. However, for highly conducting ionic fluids (such as aqueous salts like aqueous NaCl, aqueous bases like aqueous KOH, and aqueous acids like aqueous sulfuric acid) much larger inter-

electrode separations can be used without adversely effecting charge and discharge rates.

Various inorganic and organic liquid, gel, and solid electrolytes can be used for preferred invention embodiments. Generally, liquid electrolytes are optional and more preferred for the process of this invention in which charge is electrochemically induced non-faradaically in a material, and the charge and associated properties changes are retained when the electrode material is disconnected from the power source and the electrolyte is removed from the electrode material. The reason for this preference is the convenient means available for removal of liquid electrolytes from the charge-injected material without eliminating the charge injection (such as simple evaporation of the solvent component of the electrolyte). On the other hand, solid-state electrolytes are optional and more preferred for devices that retain the used electrolyte, since the use of solid-state electrolytes eliminates the problems of liquid electrolyte containment and incompatibility with the generic strategies conventionally used for device fabrication. There are tradeoffs between these different electrolyte types with respect to the allowable temperature and voltage operating ranges and the obtainable electrical conductivities. An electrolyte that is optional and preferred (because of its low cost and high ionic conductivity) is water containing simple salts, like 1 M NaCl or 1 M KCl. Other very high ionic conductivity electrolytes (like concentrated aqueous KOH and sulfuric acid) are also optional and preferred for to provide rapid charging and discharge. Aqueous electrolytes comprising at least about 4 M aqueous H_2SO_4 or 4 M aqueous KOH are especially preferred for application embodiments where the electrolyte is used only for materials processing by charge injection. Aqueous electrolytes comprising about 38 weight percent H_2SO_4 and electrolytes comprising above 5 M aqueous KOH are most especially preferred. For applications where a large degree of charge injection is needed, electrolytes with large redox windows are optional and preferred. Optional and most preferred organic electrolytes include propylene carbonate, ethylene carbonate, butylene carbonate, diethyl carbonate, dimethylene carbonate, and mixtures thereof with salts such as $LiClO_4$, $LiAsF_6$, $LiPF_6$, $LiBF_4$, $LiCF_3SO_3$, $Li(CF_3SO_2)_2N$, and $Li(CF_3SO_2)_3C$. Ionic liquid electrolytes (like 1-butyl-3-methyl imidazolium

tetrafluoroborate) and ionic liquids in polymer matrices are especially preferred because of the achievable wide redox stability range and the cycle life that they provide for redox cycling

Solid-state electrolytes can also be used advantageously, since such electrolytes enable all-solid-state devices. Optional and more preferred organic-based solid-state electrolytes are polyacrylonitrile-based solid polymer electrolytes (with salts such as potassium, lithium, magnesium, or copper perchlorate, $LiAsF_6$, and $LiN(CF_3SO_2)_2$). Optional and more preferred organic solvents for these solid-state and gel electrolytes include propylene carbonate, ethylene carbonate, γ-butyrolactone, and mixtures thereof. Optional and preferred gel or elastomeric solid electrolytes include lithium salt-containing copolymers of polyethylene oxide (because of high redox stability windows, high electrical conductivities, and achievable elastomeric properties), electrolytes based on the random copolymer poly(epichloridrin-co-ethylene oxide), phosphoric acid containing nylons (such as nylon 6,10 or nylon 6), and hydrated poly(vinyl alcohol)/H_3PO_4. Other optional and preferred gel electrolytes include polyethylene oxide and polyacrylonitrile-based electrolytes with lithium salts (like $LiClO_4$) and ethylene and propylene carbonate plasticizers. The so called "polymer in salt" elastomers (S. S. Zhang and C. A. Angell, J. Electrochem. Soc. **143**, 4047 (1996)) are also optional and preferred for lithium-ion-based devices, since they provide very high lithium ion conductivities, elastomeric properties, and a wide redox stability window (4.5-5.5 V versus Li^+/Li). Optional and preferred electrolytes for high temperature device applications include ionic glasses based on lithium ion conducting ceramics (superionic glasses), ion exchanged β–alumina (up to 1,000°C), CaF_2, and ZrO_2/Y_2O_3 (up to 2,000°C). Other optional and preferred inorganic solid-state electrolytes are AgI, $AgBr$, and Ag_4RbI_5. Optional and preferred inorganic molten salt electrolytes for high temperature devices include alkali metal halides (such as $NaCl$, KCl, and mixtures of these salts) and divalent metal halides (such as $PbCl_2$). Some of the proton-conducting electrolytes that are useful in invention embodiments as the solid-state electrolyte include, among other possibilities, Nafion, S-PEEK-1.6 (a sulfonated polyether ether ketone), S-PBI (a sulfonated polybenzimidazole), and phosphoric acid complexes of

nylon, polyvinyl alcohol, polyacryamide, and a polybenzimidazole (such as poly[2, 2'-(m-phenylene)-5,5'-bibenzimidazole].

The devices of preferred embodiments can use either one electrolyte of more than one electrolyte. For example, the electrolyte that contacts part of a porous nanostructured electrode can be different from the electrolyte that further provides an ion conducting path between electrodes. Also, different electrolytes can be used as contacting materials for different electrodes. Employing more than one electrolyte can be used to optimize device operation. For instance, a particular electrolyte (or electrolytes) can be chosen for optimizing either double-layer formation or electrode ionic conductivity. While the electrolyte that separates electrodes is preferably substantially electronically insulating, the electrolyte that contacts an individual electrode can have a significant degree of electronic conductivity. In fact, conducting polymers are used as the electrode conducting element for certain described invention embodiments. Like electrolytes, these conducting polymers can provide ion conduction and serve as an ion source. However, unlike electrolytes, these conducting polymers are electronically conducting. Hence, it is preferable that these conducting polymers do not provide an uninterrupted electronic path between opposite electrodes. For this reason, conducting polymers (or other ion-intercalated electronic conductors are optionally and preferably used in combination with one or more electronically insulating electrolyte to form a inter-electrode pathway that is largely interrupted for inter-electrode electronic transport, but maintained for inter-electrode ion transport.

The following examples are presented to more particularly illustrate the invention, and should not be construed as limiting the scope of the invention.

EXAMPLE 1

This example shows that we can continuously vary the electrical conductivity of carbon nanotube electrode sheets by about an order of magnitude using predominately non-faradaic electrochemical charge injection in 1 M NaCl electrolyte

These nanotube sheets are fabricated analogously to a previously described method (A. G. Rinzler *et al.*, Appl. Phys. A 67, 29 (1998)) by dispersing the carbon nanotubes in surfactant-containing aqueous solution and filtering this nanotube dispersion though through a 47 mm diameter poly(tetrafluoroethylene) filter sheet (Millipore LS) under house vacuum. A sheet of nanotubes collected on the filter paper, which was washed using water and methanol, dried, and then lifted from the filter paper substrate to provide a free-standing SWNT sheet. The density of these nanotube sheets is about 0.3 gm/cm^3, versus the density of about 1.3 gm/cm^3 for densely packed nanotubes having close to the observed average nanotube diameter. Hence the void volume in these nanotube sheets is about 76.9 volume percent. This high void volume, and the correspondingly high accessible surface area, is generally important for achieving high degrees of non-faradaic change injection. Supporting this conclusion, the measured BET surface area determined from nitrogen gas adsorption for these nanotube sheets is approximately 300 m^2/gm.

Two carbon nanotube electrodes (one small: ~10mm wide and ~30mm long and the other large: ~1mm wide and ~30mm long) were cut from free-standing carbon nanotube sheets made by the above described method. For the purpose of making four-probe electrical conductivity measurement, four in-series electrical contacts were made to the small carbon nanotube electrode. Gold wire (0.0127mm diameter) was attached using heat cured conductive epoxy (H20E, Epoxy Technology), which was cured at 70°C for four hours. The area of electrical contact was covered by chemically resistive epoxy (Eccobond A 316, Emerson & Cuming) in order to protect the electrical contact from exposure to subsequently used electrolytes. One electrical contact was similarly made to the large carbon electrode.

The small carbon nanotube electrode with four-probe contacts, the large carbon nanotube electrode having one electrical contact, and the Ag/AgCl reference electrode were immersed in 1M aqueous NaCl. This selected configuration (with the larger electrode about ten times smaller than the larger electrode) keeps the potential of the bigger electrode almost constant as a potential difference is applied between the small electrode (working electrode) and the large electrode (working electrode), to thereby

change the potential of the of the small electrode relative to reference electrode. The four-point electrical conductivity of the small electrode was measured as a function of the potential of this electrode with respect to the Ag/AgCl reference electrode.

Multiple experiments using the above described method provided the following results. When the potential of the carbon nanotube paper electrode (versus Ag/AgCl) was in the range of about –0.35 to about –0.50V, the conductivity showed the minimum of 60-100 S/cm. This conductivity for an uncharged carbon nanotube sheet monotonically increased up to about 1000 S/cm when the applied potential was increased to above +0.9V, and it monotonically increased up to about 250 S/cm when the potential was decreased to below –0.9V. The dependence of conductivity change upon potential (versus Ag/AgCl) was quite symmetric with respect to the potential at which the conductivity minimum occurs (at between about -0.35 about -0.50V).

Cyclic voltammetry in this potential range shows that there are no noticeable peaks due to Faradaic processes in the utilized potential range, indicating that the major electrical conductivity increases (up to an order of magnitude) are the result of predominately non-faradaic charging.

EXAMPLE 2

This example demonstrates that tuning the electrical conductivity of single-wall nanotube sheets over an order-of-magnitude range can also be accomplished using an organic electrolyte, instead of the aqueous electrolyte of Example 1.

The experimental procedure was exactly the same as for Example 1, except that the 1M NaCl aqueous electrolyte was replaced with either 0.1M $TBAPF_6$ (tetrabutyl ammonium hexafluorophosphate) or 0.1M $TBABF_4$ (tetrabutyl ammonium tetrafluoroborate) dissolved in acetonitrile and the Ag/AgCl reference electrode was replaced with the Ag/Ag^+ reference electrode. There was no significant differences noted between charge-injection tuning of the nanotube sheet conductivity in 0.1M $TBAPF_6$/acetonitrile and in 0.1 M $TBABF_4$/acetonitrile.

Because the potential window of non-faradaic reaction in non-aqueous electrolyte is much wider than for aqueous electrolytes, the potential can be changed up

to +1.0V (versus Ag/Ag$^+$) in the positive potential direction, resulting in a maximum electrical conductivity of above 1000 S/cm at these positive potentials. In the negative potential direction, non-faradaic charging was possible down to −1.5V (versus Ag/Ag$^+$), resulting in a maximum electrical conductivity of about 600-700 S/cm at these negative potentials (where electrons are being injected into the nanotubes). The minimum value was ~100 S/cm near −0.3V (versus Ag/Ag$^+$).

Figure 1 shows the presently observed continuous tunability of four-point electrical conductivity as a function of applied potential (versus Ag/Ag+) for a sheet of single-wall carbon nanotubes immersed in one of these organic electrolytes (0.1M tetrabutylammonium hexafluorophosphate in acetonitrile). These results show that the electrical conductivity can be increased by over an order of magnitude by electrochemical charge injection. There is slight hysteresis evident for the curves in Figure 1, with the conductivity σ on the extreme left side of the potential minimum slightly higher for hole injection (increasingly positive applied potential) and the conductivity slightly lower on the extreme right side of the minimum for electron injection (increasingly negative applied potentials). The different curves are for three successive cycles (using squares (101), circles (102), and triangles (103) for successive cycles).

Figure 3 shows measured cyclic voltametry during charge injection for the above SWNT sheet when immersed in the above tetrabutylammonium hexafluorophosphate electrolyte. The absence of major peaks in this cyclic voltametry curve (measured versus Ag/Ag+) indicates that charging is predominately non-faradaic for this electrolyte and potential range.

EXAMPLE 3

This example shows that the hysteresis in properties tuning can be greatly significantly reduced if electrical conductivity is varied by charging the amount of injected charge, as opposed to being controlled by changing applied voltage. This point is illustrated for the 0.1M tetrabutylammonium hexafluorophosphate/acetonitrile electrolyte by comparing the hysteresis in the electrical conductivity versus potential (Figure 1 and Example 1) with those in Figure 2, where electrical conductivity is plotted

versus charge per carbon in the nanotube working electrode. The decrease that we obtain in hysteresis in going from voltage control of conductivity to charge control is even larger for the aqueous 1 M NaCl electrolyte of Example 1. The data in Figure 2 also shows the dependence of four-point electrical conductivity upon the amount of injected charge (per carbon) for the nanotube sheet is nearly identical for the 1 M NaCl electrolyte of Example 1 and the 0.1M tetrabutylammonium hexafluorophosphate/acetonitrile electrolyte of Example 2. For the results in Figure 2, the black data points are for experiments using 0.1M tetrabutylammonium hexafluorophosphate/acetonitrile electrolyte and near-white data points are for measurements using 1 M aqueous NaCl electrolyte. The origin of the charge/carbon scale in Figure 2 is arbitrary.

EXAMPLE 4

The surprising results of this example shows that charge non-faradaically injected into carbon nanotube sheets is retained in large part when the carbon nanotube sheet disconnected from the power source, and then dried in either air or in flowing nitrogen gas. This retention of injected charge is indicated by substantial retention of the electrical conductivity enhancement caused by charge injection.

The nanotube sheet preparation and the method of charge injection and conductivity measurement is the same as in the above examples. The electrolyte used is the 0.1M tetrabutylammonium hexafluorophosphate/acetonitrile of Examples 2 and 3.

Figure 4 shows that the dramatic hole-injection-induced increase in electrical conductivity of the nanotube sheet in Figure 1 and 2 is largely retained when the hole-injected electrode is dried in flowing dry nitrogen atmosphere to remove the electrolyte. The insert to this figure shows results over a four-hour period on an expanded time scale. Figure 5 shows the retention of conductivity enhancement when the nanotube sheet is removed from the electrolyte and held in air for the investigated five day period.

EXAMPLE 5

This example demonstrates the generality of our process of non-faradaically injecting charge in a nanostructured material, and maintaining this injected charge and associated properties changes when the charge injected material is removed from the electrolyte and dried. More specifically we here show that charge non-faradaically injected into platinum nanoparticle pellets is substantially maintained even after disconnecting the platinum pellets from the power source, their removal from the electrolyte, and exposure of these pellets to a dynamically pumped vacuum for a week.

The platinum nanoparticles pellets investigated here were made at room temperature by compaction of 30 nm platinum nanoparticles. This method used for making the investigated pellets is like that described by J. Weissmüller et al. in Science 300, 312 (2003). The method that we use for attaching electrodes to the platinum pellets is the same as described in Example 1 for the carbon nanotube sheets.

The density of these Pt pellets were low (2.74 to 2.96 gm/cm^3 for an applied compaction pressure of about 0.6 to 1 MPa and 3.71 to 3.75 gm/cm^3 for an applied compactions pressure of about 2.1 MPa) as compared with the density of solid Pt (21.45 gm/cm^3). These densities correspond to a volume void space in the Pt pellets of between 81.6 and 87.2 volume percent. This high volume fraction of void space and the corresponding high gravimetric surface area explains the high degree of non-faradaic charge injection that results for modest applied potential for the Pt electrode.

Figure 6 provides cyclic voltametry measurements (20 mV/sec using 1 M aqueous NaCl electrolyte) for nanostructured platinum electrodes, showing that charging is predominately by double-layer charge injection, which is a non-faradaic process. There are no current peaks due to Faradaic processes and the current at constant voltage scan rate (20 mV/sec) varies little with potential. From plots of current versus potential scan rate in 1 M aqueous NaCl electrolyte), the electrode capacitance is about 14.5 F/gm.

Most important, we find that the nanoporous Pt electrode remains charged when disconnected from the power source, removed from the electrolyte, and dried. Indication of this retained charge is provided by reimmersion of the nanoporous Pt electrode in the 1 molar NaCl electrolyte, and finding that the electrode potential is

substantially unchanged. Our initial results indicating this stability are shown in Figure 7. Just like the case for the carbon nanotube electrode, the potential of the negatively charged electrode is less stable than for the positively charged electrode, as indicated by the results shown in the lower part of this figure.

Since it is possible that some electrolyte is still retained inside the pores of the Pt electrode during the experiment of Figure 7, we repeated this experiment using much longer time periods after the pellet electrodes have been disconnected from the power source and the electrolyte was removed from the electrochemical cell. The electrode potentials (versus Ag/AgCl) before after this two days exposure of the electrodes to dynamic vacuum pumping were +0.58 V and +0.45 V for the hole-injected electrode and -0.04 V and +0.02 for the electron-injected electrode. The potential between the two electrodes changed from the initial 0.62 V to a final 0.43 V after removal of the electrodes from the electrolyte and applying a dynamic vacuum on these electrodes for two days.

To further evaluate the stability of charge storage, we extended the time period in which we exposed the platinum pellets to dynamic vacuum to a week. After this, which we reimbursed the Pt electrodes in the 1 M NaCl electrolyte to determine their charge state by electrochemical potential measurements (naturally, without applying any external potential). High charge storage is again indicated for the positively charged Pt electrode (indicated by retention of a 0.28 V potential, versus Ag/AgCl, compared with the potential immediately before electrolyte removal of 0.33 V). The negatively charged electrode had lower stability, as indicated by a potential change from the initial -0.68 V (before removal of the electrolyte and the week-long process of drying the electrode in dynamic vacuum) to a final potential on initial reimmersion into the electrolyte of –0.32 V.

EXAMPLE 6

This examples shows that we substantially retain crystal volume expansions induced by non-faradaic charge injection even after the charge injected material is disconnected from the electrical power source, removed from the electrolyte, and dried

for two days in dynamically pumped vacuum. The implications of this discovery are broad, since minor changes in crystal unit cell volume and dimensions can cause major changes in properties like ferromagnetism and superconductivity.

We investigated a nanoporous Pt sample of Example 5, which had been non-faradaically injected with double layer charge in 1 M NaCl electrolyte and then disconnected from the power source and dried during two days exposure to dynamic vacuum pumping. The unit cell volume of the positively charge-injected electrode, determined in air by x-ray diffraction, was 1.2% larger in unit cell volume than for an identical pellet of nanoporous Pt which had not undergone the charge injection and charge stabilization process.

While it is known that charge injection in a liquid electrolyte can provide changes in unit cell volume, the prior art did not anticipate that these charge-induced volume changes can be retained in electrolyte-free materials (J. Weissmüller *et al.*, Science **300**, 312 (2003) and R. H. Baughman, Science **300**, 268-269 (2003)).

The invention being thus described, it will be obvious that the same may be varied in many ways. Such variations are not to be regarded as a departure from the spirit and scope of the invention, and all such modifications as would be obvious to one skilled in the art are intended to be included within the scope of the following claims.

What is claimed is:

1.   A process to provide, retain and employ charge injection to substantially change the properties of a largely electrolyte-free porous material region A or particle A that comprises:

    (a) immersing the A into an electrolyte;

    (b) providing an ion conducting and substantially electronically insulating continuous path between the A and a counter-electrode material B;

    (c) applying a potential between the A and the counter electrode B for sufficient time that substantial charge is injected into the A; and

    (d) substantially removing the electrolyte from contact with the A,

wherein both the A and the counter electrode B have an electronically conducting charged or uncharged state and the A has an achievable capacitance for non-faradaic charging of above about 0.1 F/gm.

2.   The process of claim 1, wherein the thickness of the material region A is less than about a centimeter.

3.   The process of claim 1, wherein the thickness of the material region A is less than about 1000 microns.

4.   The process of claim 1, wherein the thickness of the material region A is greater than about 10 microns.

5.   The process of claim 1, wherein, in step (c), the material region A is cyclically charged and discharged before a final charging step.

6.   The process of claim 1, wherein in step (c), resistance compensation is used to accelerate the rate charge is injected.

1   7.   The process of claim 1, wherein the A comprises a substance selected from the
2   group consisting of nanofibers, an aggregate of electronically conducting particles, a
3   direct photonic crystal that is electronically conducting, and an inverse photonic crystal
4   that is electronically conducting.

1   8.   The process of claim 6, wherein the A comprises carbon nanotubes.

1   9.   The process of claim 8, wherein said carbon nanotubes are configured as a
2   porous sheet or a porous fiber.

1   10.   The process of claim 1, wherein the A is a particle.

1   11.   The process of claim 1, wherein the A has a gravimetric capacitance of at least 1
2   F/gm.

1   12.   The process of claim 1, wherein the A has a surface area of at least about 0.1
2   m^2/gm.

1   13.   A composition of matter comprising non-faradaically injected charge and
2   substantially no electrolyte that maintains, in a suitable environment, a potential that
3   deviates from the potential of zero change by at least 0.1 V.

1   14.   The macroscopic composition of matter made by the process of claim 11 that
2   maintains, in a suitable environment, a potential that deviates from the potential of zero
3   change by at least 0.4 V.

1   15.   A composition of matter made by the process of claim 11 that has macroscopic
2   size in all three dimensions.

1   16.   A device having tunable response that comprises:
2   (a) a nanostructured electrode component C of a first electrochemical electrode
3   and a electrode component D of a second electrochemical electrode;

4   (b)   an ionically conducting material that is substantially electronically non-
5   conducting that connects said first and said second electrochemical electrodes;
6   and
7   (c) means to provide a voltage between said first and said second
8   electrochemical electrodes,
9 wherein the electrode component C is not in direct contact with an electrolyte, the
10 electrode component C has an achievable capacitance of above about 0.1 F/gm for
11 substantially non-faradaic charging, and wherein properties changes of the electrode
12 component C in response to injected charge are used to achieve device performance.

1   17.   The device of claim 16 that provides a process selected from the group
2 consisting of electromechanical actuation, the controlled storage and release of
3 synthetic or biologically derived materials, conversion of mechanical energy to electrical
4 energy, conversion of photonic energy to electrical energy, conversion of electrical
5 energy to mechanical energy or mechanical displacement, conversion of thermal
6 energy to electrical energy using thermoelectric, thermoelectrochemical, or thermoionic
7 effects, conversion of chemical energy to electrical energy in a fuel cell, stress or strain
8 sensing, chemical and biochemical sensing, wherein the device response is at least in
9 part effected by a change in the degree of non-faradaic charge injection in the electrode
10 component C.

1   18.   A device of claim 17 that functions at least in part in response to application of
2 an electrical voltage between said first and second electrochemical electrodes.

1   19.   A device of claim 16, wherein electrode component C comprises a substance
2 selected from the group consisting of nanofibers, an aggregate of electronically
3 conducting particles, a direct photonic crystal that is electronically conducting, and an
4 inverse photonic crystal that is electronically conducting.

1   20.   The device of claim 19, wherein electrode component C comprises electronically
2 conducting particles, wherein these electronically conducting particles are selected from

3   the group consisting of an elemental metal, an elemental metal alloy, and a substance
4   coated with an elemental metal or elemental metal alloy, and wherein these
5   electronically conducting particles are percolated with themselves to provide a
6   continuous path for electronic conductivity within the electrode component C.

1   21.   The device of claim 20, wherein said electronically conducting particles are
2   configured as a photonic crystal.

1   22.   The device of claim 19, comprising an electronically conducting inverse-lattice
2   photonic crystal.

1   23.   A device of claim 19, wherein said nanofibers in electrode component C
2   comprise a substance selected from the group consisting of single-wall, multi-wall, of
3   scrolled carbon-containing nanotubes.

1   24.   A device of claim 20, where each of the first and second electrochemical
2   electrodes comprise a substance selected from the group consisting of nanofibers, an
3   aggregate of electronically conducting particles, a direct photonic crystal that is
4   electronically conducting, and an inverse photonic crystal that is electronically
5   conducting.

1   25.   A device of claim 16, wherein each of said first electrochemical electrode and
2   said second electrochemical electrode have a maximum achievable electronic
3   conductivity of at least about 1 S/cm and wherein the ratio of the maximum electronic
4   conductivity of a highest conductivity electrode to the electronic conductivity of the
5   electrolyte that is ionically conducting and electronically insulating is at least about 10^5.

1   26.   A device of claim 16, wherein exactly one of said first and said second
2   electrochemical electrodes is capable of undergoing substantial intercalation with ions.

27. A device of claim 16, in which the first electrochemical electrode undergoes predominately non-faradaic charging and the second electrochemical electrode undergoes predominately faradaic charging during normal device operation.

28. A device of claim 16, comprising at least one electrolyte within the ion conducting path between said first and said second electrochemical electrode, wherein said electrolyte is selected from the group consisting of an aqueous salt solution of either an alkali metal cation and a halogen anion, a ceramic solid state electrolyte, a polymer solid-state electrolyte, an ionic liquid of ionic liquid in a polymer matrix, and either sulfuric acid or KOH having a molar concentration above 4 M.

29. A device of claim 16, wherein said first electrochemical electrode additionally comprises a faradaic component that undergoes predominately faradaic charging by intercalation during device operation, wherein the intercalated state is electronically conducting, wherein said electrode component C of the said first electrochemical electrode contacts this faradaic component, and wherein said electrode component C of the said first electrochemical electrode has a void volume of at least about 25%.

30. A device of claim 29, wherein said electrode component C has a void volume of at least about 50%.

31. A device of claim 30, wherein said electrode component C has a void volume of at least about 75%.

32. A device of claim 16, wherein said first electrochemical electrode additionally comprises a faradaic component that undergoes predominately faradaic charging by intercalation during device operation, wherein the intercalated state is electronically conducting, wherein said electrode component C of the said first electrochemical electrode contacts this faradaic component, and wherein a solid-state electrolyte contacts this faradaic component.

1   33.   A device of claim 16, wherein said first electrochemical electrode additionally
2   comprises a faradaic component that undergoes predominately faradaic charging by
3   intercalation during device operation, wherein the intercalated state is electronically
4   conducting, wherein said electrode component C contacts the faradaic component, and
5   wherein the faradaic component is selected from the group consisting of an inorganic
6   polymer, a sheet-containing material, and a nanofiber-containing material.

1   34.   A device of claim 16, wherein said first electrochemical electrode additionally
2   comprises a faradaic component that undergoes predominately faradaic charging by
3   intercalation during device operation, wherein the intercalated state is electronically
4   conducting, wherein said electrode component C contacts this faradaic component, and
5   wherein said second electrochemical electrode has at least about ten times the volume
6   of the said first electrochemical electrode.

1   35.   A device of claim 17 for converting electrical energy to mechanical energy or
2   mechanical displacement, wherein at least partially reversible mechanical displacement
3   results from charge injection into electrode component C.

1   36.   A device of claim 17 for stress or strain sensing or for converting mechanical
2   energy to electrical energy that operates at least in part from the electrochemical
3   potential change of electrode component C in response to an applied stress.

1   37.   A fuel cell device of claim 17, wherein fuel cell redox reactions occur at electrode
2   component C in the substantial absence of contacting electrolyte.

1   38.   A fuel cell device of claim 37, wherein electrode component C comprises a
2   catalyst and electrode component C is separated from the second electrochemical
3   electrode by a solid-state ionic conductor having low permeability for the fuel
4   components used for fuel cell operation.

1   39.   A device of claim 17 for conversion of thermal energy to electrical energy using
2   the thermoelectric effect wherein electrode component C comprises a porous

3   thermoelectric, the electrode component C is substantially not contacted by electrolyte,

4   and non-faradaic charge injection in electrode component C is used to optimize the

5   thermal Seebeck coefficient.

1   40.   A device of claim 16, further comprising a third electrochemical electrodes,

2   wherein the first, second, and third electrochemical electrodes are charged during

3   device operation.

1   41.   A device of claim 16, further comprising a reference electrode.

1   42.   A device of claim 16, wherein the shortest length path for ion transport between

2   the first and second electrochemical electrodes is at most about 1000 microns.

1   43.   A device of claim 42, wherein the shortest length path is at most about 100

2   microns.

1   44.   A device of claim 43, wherein the shortest length path is at most about 10

2   microns.

1   45.   A device of claim 16, wherein the first electrochemical electrode has microscopic

2   dimensions.

1   46.   A device of claim 16, wherein said first electrochemical electrode comprises a

2   single nanofiber or nanofiber bundle that is less than 80 nm in largest diameter.

1   47.   A device of claim 16, wherein the second electrochemical electrode has at least

2   about a hundred times the volume of the first electrochemical electrode.

1   48.   A device of claim 47, wherein the second electrochemical electrode has at least

2   about ten times the volume of the first electrochemical electrode.

1   49.   A device of claim 16, that is a chemical sensor, wherein a gas phase component
2   is sensed at least in part by the change in the resistance of an electrode component C.

1   50.   A device of claim 14, that is a gas sensor, wherein a gas phase component is
2   sensed at least in part by measuring the current between said first electrochemical
3   electrode and said second electrochemical electrode as a function of the potential of
4   said electrode component C.

1   51.   A device of claim 50, further comprising a solid-state electrolyte and a reference
2   electrode inserted in an electrolyte, wherein the potential of said electrode component
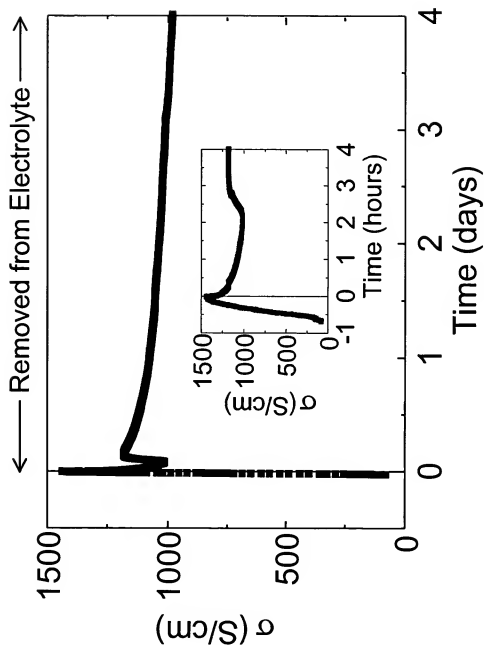3   C is measured with respect to the reference electrode during the device operation.
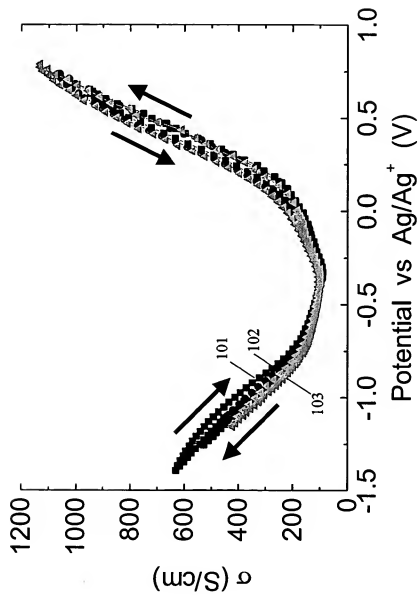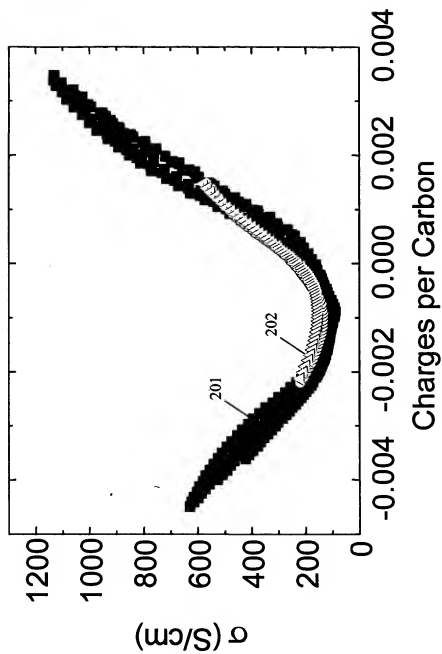
Fig. 1

Fig. 2

Fig. 3

Figure 4
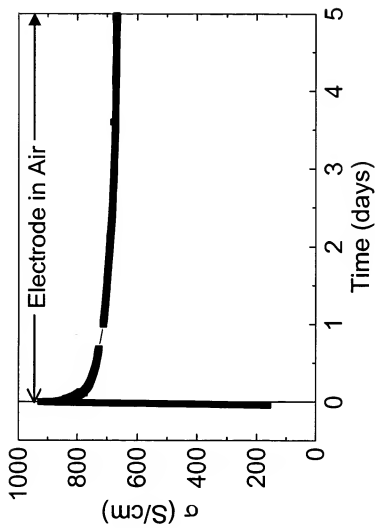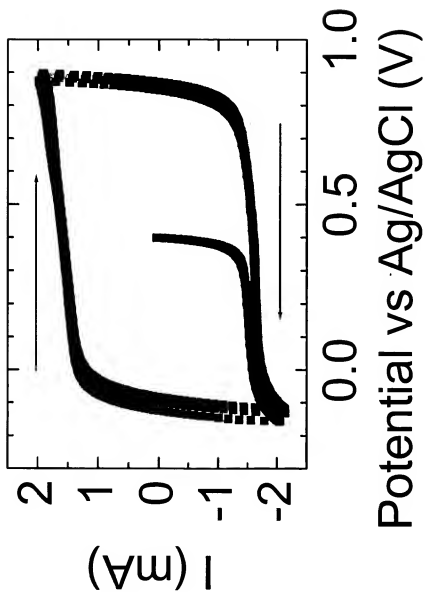
Fig. 5

Fig. 6
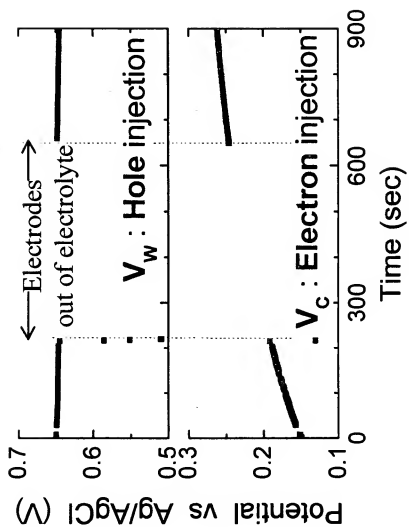
Figure 7
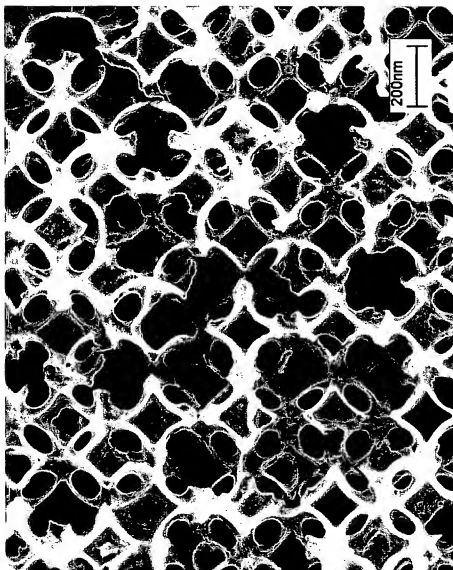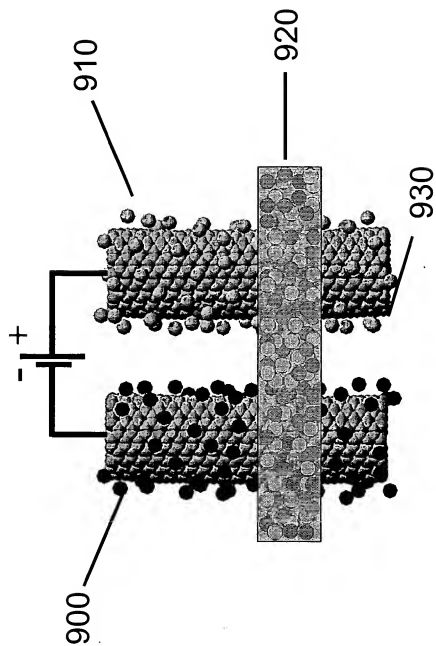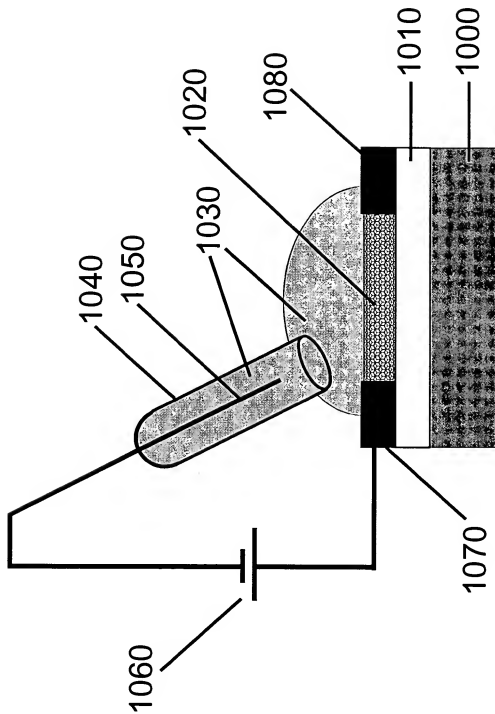
200nm

Fig. 8

910

920

930

900

Fig. 9

Fig. 10 (Prior art)
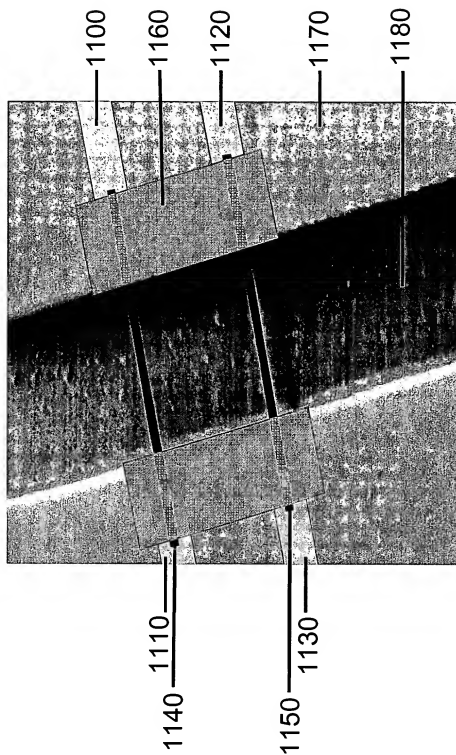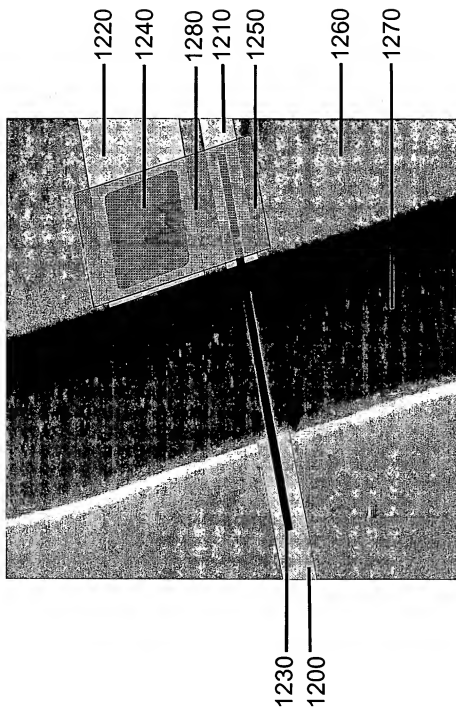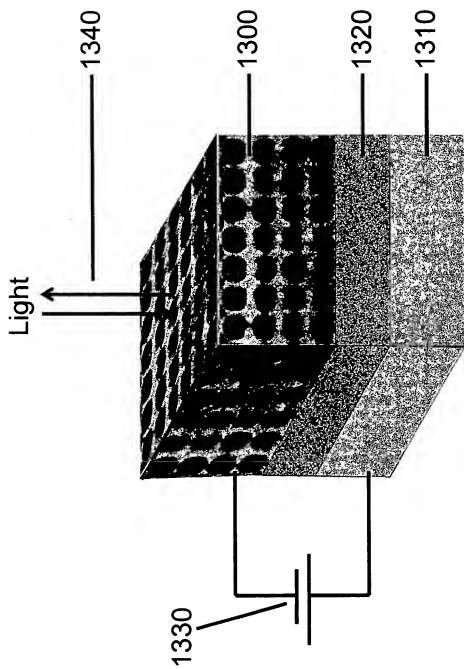
1010
1000
1020
1080
1030
1040
1050
1070
1060

Fig. 11

Fig. 12

1220
1240
1280
1210
1250
1260
1270
1230
1200

Light

1340

1300

1320

1310

1330

Fig. 13

APPLICATION DATA SHEET

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Application Information: Title: MATERIAL   AND   DEVICE   PROPERTIES
                                  MODIFICATION BY ELECTROCHEMICAL CHARGE
                                  INJECTION IN THE ABSENCE OF CONTACTING
                                  ELECTROLYTE FOR EITHER LOCAL SPATIAL OR
                                  FINAL STATES
                           Classification: Class: Subclass:
                           Tech Center:
                           Drawing Sheets: 13   Drawing to be Published: 9
                           Docket No: 13991-P003V1
                           Type: Provisional
                           Secrecy: None

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                                Richard F. Frankeny, Reg. No. 47,573

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Domestic Priority:

Application:	Continuity Type:	Parent Application:	Parent Filing Date:

Foreign Priority Information

Country:	Application Number:	Filing Date:	Priority Claimed:

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